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# TECHNO-ECONOMIC STUDY OF BIO-ETHANOL PRODUCTION AS A CARBON CAPTURE AND UTILIZATION PROCESS

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# ABSTRACT

Paula Kosonen: Techno-economic study of bioethanol production as a carbon capture and utilization process
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Climate change is proceeding rapidly, and the main challenge are the anthropogenic carbon dioxide ($CO_2$) emissions. If nothing is changed during the next few years, the consequences for the global society will be massive. Unfortunately, there are no single or simple solutions to reaching international energy and climate goals. The most efficient solution will consist of several technologies which are adopted simultaneously. One of the potential technologies is carbon capture and utilization (CCU), in which $CO_2$ from point sources or directly from air is utilized as raw material to produce fuels, chemicals, and materials. If the captured $CO_2$ is biogenic, it is possible to reach even negative carbon balance and at the same time the final products are considered bioproducts.

The aim of this thesis was to investigate potential CCU technologies for biogenic $CO_2$ originating from flue gases. The study was carried out as a literature survey and techno-economic analysis of the scientific articles, books and technical reports. The major post-combustion carbon capture technologies utilize absorption, adsorption, cryogenic distillation, membranes or biological techniques. Currently, the only commercially used method is the amine-based chemical absorption. However, it is an expensive process and therefore new alternatives are searched. One potential alternative, which was also selected to the techno-economic analysis, is absorption with potassium carbonate solvent. The reaction rate of the process is, however, slow and therefore an effective promoter, such as carbonic anhydrase enzyme, is required to make the process feasible.

The $CO_2$ utilization technologies can be divided into chemical and biological conversion, mineralization and direct utilization. Here, the focus was especially on the process, where the captured $CO_2$ is used to produce bioethanol through gas fermentation. Ethanol is a primary alcohol, which has numerous applications both in chemical industry as a building block or solvent and fuel. Therefore, the global ethanol market is significant. In gas fermentation, acetogenic bacteria convert gaseous substrate, such as $CO_2$ or carbon monoxide, to ethanol and acetate, for instance. Since possible origins for the gas substrate in addition to captured $CO_2$ include syngas from gasification of biomass or municipal solid waste, exhaust gas from steel production and reformed biogas, gas fermentation is a potential technology for broader circular economy systems as well.

In the techno-economic analysis, a process converting biobased $CO_2$ from a pulp mill to industrial grade bioethanol through gas fermentation was investigated. The process consists of five unit processes, which are carbon capture, water electrolysis, reverse water gas shift, gas fermentation, and product recovery. Through these unit processes, the $CO_2$ is first captured from the flue gas, combined with renewable hydrogen ($H_2$) and converted to syngas, which is then fermented to aqueous ethanol broth and finally the ethanol is recovered from the broth with distillation and molecular sieves to obtain anhydrous ethanol. The process produces 280 L ethanol per captured $CO_2$ ton. In the base case, the obtained levelized cost was 0.98 €/L, which is high in comparison with the current market prices. When the process parameters were optimized, the levelized cost of 0.54 €/L was obtained. It is a more promising result, but the payback period of the process, 6.5 years, is still too high for a feasible investment. However, most of the costs are caused by the water electrolysis unit. The $H_2$ production accounts for 75 % of operational and 58 % of capital expenses. If the electrolysis unit is replaced with a more cost-efficient $H_2$ production method, the studied process may be economically feasible. However, despite the fact, that the production of renewable $H_2$ is a widely examined research topic, the breakthroughs keep researchers waiting.

Keywords: carbon capture and utilization (CCU), carbon dioxide, bioethanol, absorption, gas fermentation, techno-economic analysis

# TIIVISTELMÄ

Paula Kosonen: Teknoekonominen analyysi bioetanolin tuotannosta hiilidioksidin talteenotto- ja hyötykäyttöprosessina
Diplomityö
Tampereen yliopisto
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Ilmasto lämpenee ihmisen aiheuttamien päästöjen vuoksi nopeasti ja jos asiaan ei puututa, seuraukset koko ihmiskunnalle ovat mittavat. Globaaleja ilmastotavoitteita ei kuitenkaan saavuteta vain yhden teknologian avulla, vaan tehokkain ratkaisu on yhdistelmä monien eri menetelmien samanaikaista hyödyntämistä. Yksi potentiaalisista teknologioista on hiilidioksidin talteenotto ja hyödyntäminen (CCU), jossa pistelähteistä tai suoraan ilmasta talteen otettua hiilidioksidia hyödynnetään polttoaineiden, kemikaalien ja materiaalien raaka-aineena. Jos käytetty hiilidioksidi on biopohjaista, on mahdollista saavuttaa jopa negatiivinen hiilitase ja samalla tuotetut materiaalit käsitetään biotuotteiksi.

Tämän diplomityön tarkoituksena oli tutkia potentiaalisia CCU-menetelmiä savukaasuista erotettavalle biopohjaiselle hiilidioksidille. Tutkimus toteutettiin kirjallisuuskatsauksena ja teknoekonomisena analyysina hyödyntäen tieteellisiä artikkeleita, kirjoja ja teknisiä raportteja. Pääasialliset poltonjälkeiset hiilidioksidin talteenottomenetelmät hyödyntävät absorptiota, adsorptiota, kryogeenistä tislausta, kalvotekniikoita tai biologisia menetelmiä. Näistä tällä hetkellä ainoa laajasti käytetty menetelmä perustuu kemialliseen absorptioon, jossa liuottimena käytetään erilaisia amiineja. Menetelmä on kuitenkin kallis ja ympäristölle haitallinen, joten uusia prosesseja kehitetään. Yksi potentiaalinen vaihtoehto, joka valittiin myös teknoekonomiseen analyysiin, on absorptio, jossa käytetty liuotin on kaliumkarbonaatti. Prosessi vaatii kuitenkin toimiakseen tehokkaan katalyytin, esimerkiksi hiilihappoanhydraasientsyymin. Hiilidioksidin hyödyntämismenetelmät voidaan puolestaan jakaa kemialliseen ja biologiseen konversioon, mineralisointiin ja suoraan käyttöön. Mahdollisia lopputuotteita on lukemattomia. Tässä työssä keskityttiin erityisesti prosessiin, jossa hiilidioksidista tuotetaan kaasufermentoinnin avulla bioetanolia. Etanoli on primäärisiin alkoholeihin kuuluva yhdiste, jolla on lukuisia käyttökohteita niin kemianteollisuuden raaka-aineena kuin polttoaineenakin ja siksi sen globaalit markkinat ovat merkittävät. Kaasufermentointi on menetelmä, jossa esimerkiksi asetogeeniset bakteerit muuntavat kaasumuotoisen raaka-aineen, kuten hiilidioksidin tai hiilimonoksidin, esimerkiksi etanoliksi ja asetaatiksi. Kaasufermentointi on CCU:n lisäksi lupaava menetelmä myös muihin kiertotalousprosesseihin, koska substraattikaasu voi talteen otetun hiilidioksidin lisäksi olla biomassan tai yhdyskuntajätteen kaasutuksesta syntynyttä synteesikaasua, teräksen tuotannon poistokaasuja tai reformoitua biokaasua.

Teknoekonomisessa analyysissa tutkittiin prosessia, jossa sellutehtaan meesauunista talteen otetusta hiilidioksidista tuotetaan kaasufermentoinnin avulla teollisuuslaatuista bioetanolia. Prosessi koostuu viidestä yksikköprosessista, jotka ovat hiilidioksidin talteenotto kaliumkarbonaattiabsorptiolla, vedyn valmistus elektrolyysillä, käänteinen vesikaasureaktio, kaasufermentointi sekä lopputuotteen puhdistus tislaamalla ja molekyyliseuloilla. Näiden yksikköprosessien aikana hiilidioksidi erotetaan muusta savukaasuvirrasta ja muunnetaan yhdessä vedyn kanssa synteesikaasuksi, joka konvertoidaan fermentorissa etanolivesiliuokseksi. Lopuksi liuos tislataan ja käsitellään molekyyliseuloilla, jotta ylimääräinen vesi saadaan poistettua. Prosessi tuottaa 280 litraa etanolia talteen otettua hiilidioksiditonnia kohti. Perustapauksessa etanolin tasoitetuksi kustannukseksi saatiin 0,98 €/l, joka on nykyiseen markkinahintaan verrattuna korkea. Prosessiparametreja optimoimalla saavutettiin tasoitettu kustannus 0,54 €/l, joka on lupaavampi tulos, vaikkakin projektin takaisinmaksuaika 6,5 vuotta on edelleen korkea. Kustannusten merkittävin aiheuttaja on vedyn tuotanto, joka vastaa 75 % operointi- ja 58 % kapitaalikustannuksista. Jos elektrolyysi korvataan jollakin kustannustehokkaammalla vedyntuotantomenetelmällä, prosessi voi olla kaupallisesti kannattava. Uusiutuvan vedyn tuottaminen on kuitenkin aihe, jota on tutkittu ja tutkitaan laajasti, mutta varsinaisten läpimurtojen saavuttamiseen mennee vielä vuosia.

Avainsanat: hiilidioksidin talteenotto ja hyödyntäminen (CCU), hiilidioksidi, bioetanoli, absorptio, kaasufermentaatio, teknoekonominen analyysi

# PREFACE

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Tampere, 3rd November 2020

Paula Kosonen

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# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| ADt | Air-dry pulp ton |
| BECCU | Bioenergy carbon capture and utilization |
| CA | Carbonic anhydrase |
| CAPEX | Capital expenditures |
| CCS | Carbon capture and storage |
| CCU | Carbon capture and utilization |
| CCUS | Carbon capture, utilization and storage |
| CSTR | Continuous stirred tank reactor |
| DEA | Diethanolamine |
| DGA | Diglycolamine |
| DIPA | Diisopropanolamine |
| DME | Dimethylether |
| EOR | Enhanced oil recovery |
| ESP | Electrostatic precipitator |
| FT | Fischer-Tropsch |
| IEA | International Energy Agency |
| IRR | Internal rate return |
| LCOEtOH | Levelized cost of ethanol |
| MEA | Monoethanolamine |
| MDEA | Methyldiethanolamine |
| MTBE | Methyl-tert-butylether |
| $NO_x$ | Oxides of nitrogen |
| NPV | Net present value |
| OPEX | Operational expenses |
| PC | Potassium carbonate |
| PCC | Post-combustion carbon capture |
| PCC | Precipitated calcium carbonate |
| PM | Particulate matter |
| PSA | Pressure swing adsorption |
| RWGS | Reverse water gas shift |
| $SO_x$ | Oxides of sulfur |
| TEA | Techno-economic analysis |
| TEA | Triethanolamine |
| TRL | Technology Readiness Level |
| TSA | Temperature swing adsorption |
| VTT | Technical Research Centre of Finland |
| WGS | Water gas shift |

| | | |
|---|---|---|
| $\alpha$ | scale coefficient | |
| $C$ | cost of equipment | [€] |
| $F$ | cost of feedstock | [€] |
| $E$ | cost of energy | [€] |
| $I$ | investment value | [€] |
| $i$ | inflation rate | [%] |
| $k$ | interest rate | [%] |
| $n$ | investment time | [years] |
| $O$ | operating and maintenance cost | [€] |
| $P$ | ethanol output | [L/a] |
| $R$ | revenue | [€] |
| $r$ | discount rate | [%] |
| $t$ | year | |

| | | |
|---|---|---|
| $V$ | capacity | |
| $X_t$ | net cash flow | [€] |

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# 1. INTRODUCTION

Nowadays, it is an unpleasant fact that climate change is proceeding rapidly and if nothing is changed during the next few years, the consequences for the global society will be massive. The most challenging environmental issues are greenhouse gases (GHG), from which carbon dioxide ($CO_2$) is one of the largest anthropogenic GHG sources (Meunier et al 2019). $CO_2$ is believed to be more responsible for global warming and climate change than the other greenhouse gases (water vapor, methane and nitrous oxide) due to its longer remain in the atmosphere (Aghaie et al. 2018). Unfortunately, there are no single or simple solutions to reaching international energy and climate goals. However, according to International Energy Agency (IEA 2020), Carbon Capture, Utilization and Storage (CCUS) will have a significant role in reaching net-zero emissions alongside electrification, hydrogen and sustainable bioenergy. Carbon capture is a process where gaseous $CO_2$ is separated from point sources, such as industrial flue gases, or directly from air. In this thesis, the focus is on Carbon Capture and Utilization (CCU) applications since they enable $CO_2$ valorization into value added products. In CCU, pure $CO_2$ or $CO_2$ containing gas mixtures from point sources or air are used as feedstock to produce fuels, chemicals and materials. (Onarheim et al. 2015) The point sources are typically industrial flue gases, for instance.

Our whole society is based on carbon containing fuels, materials and chemicals, and in the immediate future, the usage of these commodities is likely to remain at a significant level. Even if the global electricity supply system could be largely decarbonized, there remain significant applications, such as aviation, maritime transport and chemicals, where carbon serves an important role either as feedstock or as an energy carrier and cannot be displaced. Since these are currently made from fossil-based raw materials, the amount of emitted $CO_2$ is not going to decrease spontaneously. However, it is possible to continue the use of hydrocarbons and at the same time reduce net carbon emission to atmosphere by replacing fossil-based fuels, chemicals and materials with equivalent commodities that are made from captured $CO_2$ with low-carbon energy. (Onarheim et al. 2015) Especially, if the materials are made utilizing biogenic $CO_2$, it is possible to reach even negative $CO_2$ balance and at the same time the final products are considered bioproducts (Kuparinen et al. 2019; Kouri et al. 2017). Therefore, CCU is a

possible route to reduce the use of fossil fuels and $CO_2$ emissions and simultaneously produce sustainable bioenergy or raw materials.

The potential of CCU as a climate mitigation tool depends on the whole CCU process system, including the energy input of the process, the storage time of $CO_2$ in the product and its final use. In most $CO_2$ utilization applications, such as production of chemicals or fuels, the captured $CO_2$ is in the end released back into atmosphere. (Kouri et al. 2017; Onarheim et al. 2015) Thus, the key challenge in the field of CCU is to identify processes which are the most advanced and at the same time environmentally friendly methods. The $CO_2$ molecule contains no energy and due to the double-bond of the molecule, the conversion of $CO_2$ is highly energy-intensive meaning that the used energy source must be carefully selected. (Onarheim et al. 2015) Especially, the risk of generating new $CO_2$ emission sources and increasing energy consumption must be discussed and avoided. (Chauvy et al. 2019) However, in comparison of Carbon Capture and Storage (CCS) projects, which store the captured $CO_2$ underground permanently but are an unprofitable business that require large capital investments, CCU may be a successful business since the products can be sold (Cuéllar-Franca & Azapagic 2015).

However, markets alone will not turn CCU into a success story. Governments and industry have a significant effect on the spreading of CCU technologies, because withouth well planned politics the private business sector will not invest on CCU methods enough. (IEA 2020) One of the key strategies to $CO_2$ level decreasing is carbon pricing, either in the form of carbon allowances or a carbon tax. However, formerly the common problem has been the pricing: it has been more feasible to pay for carbon allowances than invest the construction and operating of a $CO_2$ capture system. Fortunately, little by little the gradual changes in politics have changed the situation and nowadays the interest on carbon capturing is growing. (Meunier et al. 2020) The currently utilized $CO_2$ volume is more than 200 Mt/a, from which 20 % is used directly and 80 % is converted to value added chemicals. However, most of the $CO_2$ in question is originating from the process itself, such as production of urea, or from the upstream processes, while the concepts which utilize captured $CO_2$ as a raw material are currently emerging. (Onarheim et al. 2015) Thus, the purpose of this thesis is to collect the knowledge of carbon capture and utilization technologies.

This study is restricted to the biogenic CCU applications. However, the term “biogenic” is defined liberally: the produced $CO_2$ from pulp mills is not divided into fossil and bio-based even though in some point sources the used fuel might occasionally be fossil-based. Here, all the produced $CO_2$ is considered biobased. The study consists of two sections: a literature survey and a techno-economic analysis (TEA).

In the first part, a literature survey of carbon capturing and utilization technologies is presented in aim to find out the most promising carbon capturing and carbon utilization technologies for the $CO_2$ originating from pulp mills or biomass power plants. Since a significant share of air pollution and $CO_2$ originates from combustion processes, carbon capturing is here examined as a post-combustion process. (Karaszova et al. 2020) First, the background of biogenic $CO_2$ formation in pulp mills and biomass power plants is described. After that, a general background of carbon capturing and carbon utilization technologies is discussed and then the most promising technologies have been chosen for more detailed consideration.

The second part is a techno-economic analysis of industrial grade bioethanol production through gas fermentation using captured $CO_2$ as a raw material. The studied process is selected on the basis to find a promising multifunctional process which produces end-product with various uses. The carbonic anhydrase catalyzed absorption process offers an eco-friendly carbon capturing process while gas fermentation is typically examined as a process where the raw material syngas is originating from the gasification of biomass instead of carbon capturing. Therefore, this thesis aims to offer data for the novel combination of these unit processes. First, the unit processes are described one at a time and then the equations for the calculations and the variables for the scenario analysis are presented. After that, the results are presented and critically assessed in discussion part. Finally, there are conclusions. In the techno-economic analysis, the aim is to investigate what is the levelized cost of CCU-based bioethanol and whether it is competitive in comparison with the current ethanol market prices. In the scenario analysis, process parameters are varied to find out the circumstances which lead to a feasible manufacturing process.

# 2. BIOMASS AS A $CO_2$ SOURCE IN KRAFT PULP MILLS AND BIOMASS POWER PLANTS

The main industrial sources of biogenic $CO_2$ include bioethanol production, anaerobic biogas digesters, pulp mills or biorefineries and waste-to-energy plants. Generally, the basic rule is that the higher the $CO_2$ content in the gas stream, the more efficient is the $CO_2$ capturing process. However, even though the $CO_2$ content in the gas streams from bioethanol production (close to 100 %) or anaerobic biogas digesters (35-45 %) is relatively high, the overall worldwide capacity of those industrial sectors is minor compared with pulp and paper industry which is one of the largest industrial energy users. (Olsson et al. 2020; IEA 2014)

Since the raw material used in chemical pulping is mainly woody biomass and the residues are utilized by burning, the $CO_2$ produced in pulp and paper mills is largely biogenic. (Kuparinen et al. 2019) Therefore, despite the lower $CO_2$ content (10-20 %) in the gas stream, the carbon capturing is in this thesis examined as a process which is connected to pulp and paper production. However, it is assumed that the operation of the biomass boiler in a pulp mill is similar to the operation of the biomass boiler in biomass power plants. Therefore, the parts discussing on the biomass boilers are substantially relevant to the stand-alone biomass power plants yet the used fuels may vary little.

In the kraft pulp mills, the $CO_2$ is formed primarily during combustion, when carbon in the fuel reacts with oxygen according to:

$$C + O_2 \rightarrow CO_2. \quad (1)$$

The largest point sources of $CO_2$ are the recovery boiler, the biomass boiler, and the lime kiln, from which the lime kiln is typically the only fossil $CO_2$ source under normal operating conditions. (Kuparinen et al. 2019) Figure 1 presents a simplified process diagram of the main $CO_2$ sources of a kraft pulp mill.

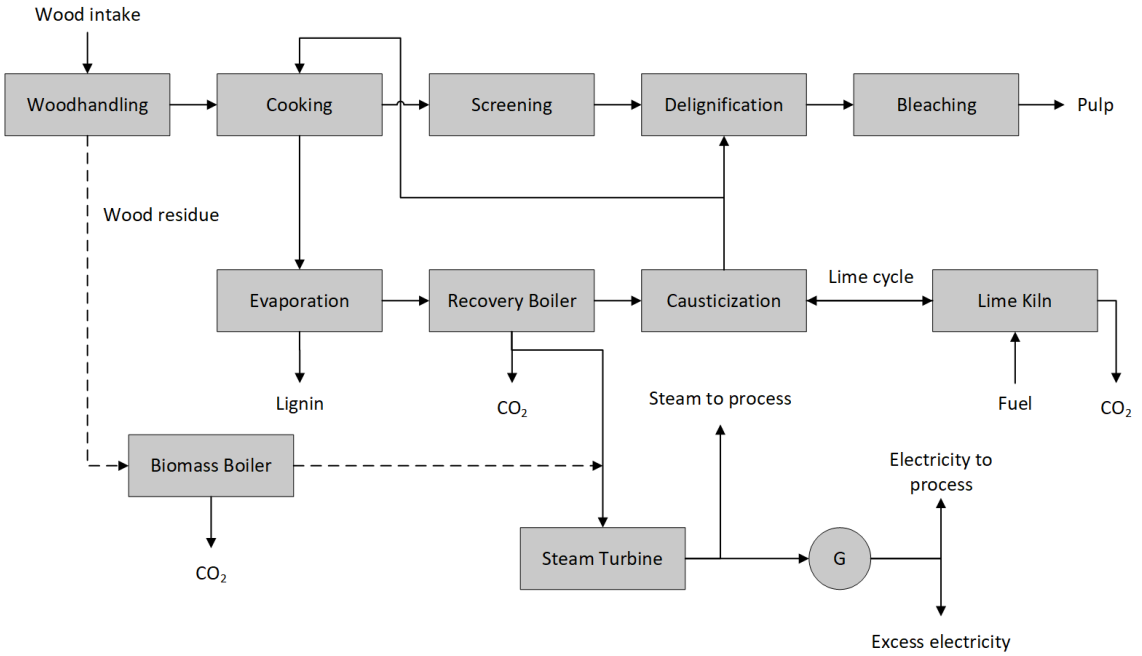



***Figure 1. Operations and $CO_2$ output streams in kraft pulp mill (adapted from Kuparinen et al. 2019).***

In the biomass boiler, the biomass residues, such as bark and fines, from the wood handling processes are utilized in the energy production. The recovery boiler is used to burn the concentrated black liquor to utilize the organic residue from pulping and recover the used sodium-based pulping chemicals. In addition to these burned materials, fossil fuels are typically used during startups and shutdowns and if auxiliary steam is needed. In the biomass boiler, the fossil fuel usage causes at least 20 kilograms (kg) $CO_2$ per air-dry pulp ton (ADt), while in the recovery boiler, fossil-based $CO_2$ production is 10-20 kg $CO_2$/ADt and the biogenic $CO_2$ production 1600-2400 kg $CO_2$/ADt. (Kuparinen et al. 2019)

The lime kiln is a part of the caustizing plant, where during the lime cycle the aim is to first convert the sodium carbonate ($Na_2CO_3$) to sodium hydroxide (NaOH) and then regenerate the reaction product calcium carbonate ($CaCO_3$) to calcium oxide (CaO). The by-product of the latter reaction is $CO_2$ as can be seen from the following reaction:

$$CaCO_3 + heat \rightarrow CaO + CO_2. \quad (2)$$

The lime kiln operation generates both biogenic and fossil $CO_2$, because fossil fuels are typically used to reach the required elevated temperature, at least 850 °C. The produced amount of fossil $CO_2$ in the lime kiln is 100-250 kg $CO_2$/ADt. (Kuparinen et al. 2019)

Even though there are multiple $CO_2$ point sources in the pulp mill, the carbon capture system would likely be installed on only one of those. If the aim is to capture biobased $CO_2$, the biomass boiler is the best option, since the $CO_2$ content of the flue gas is

relatively high and the boiler is not a critical part of the pulping process. If some problems with operating the carbon capture system occur, the whole pulping process will not be at risk for an outage. Additionally, there are biomass boilers in the pulp mills but also in the biomass power plants. If the carbon capture system is designed for one biomass boiler, it is quite easy to scale to numerous plants. However, in addition to the biomass residues, it is not uncommon to burn sludges or rejects in the biomass boiler and in that case, all the produced $CO_2$ may not be biogenic. Anyway, in related to the global warming and too high $CO_2$ content in the atmosphere, this kind of classification is artificial. When a fuel is combusted, the $CO_2$ affects the climate identically, no matter if it is biogenic or fossil-based (Mäkikouri et al. 2018). Therefore, if the aim is to capture $CO_2$ from the pulp mill efficiently, the most promising point source seems to be the lime kiln, since the $CO_2$ content of the flue gas can be two times higher than from the biomass boiler. Table 1 presents the typical compositions of the flue gases from an 85 MW biomass boiler and an 80 MW lime kiln.

***Table 1. Typical composition of flue gases from biomass boiler and lime kiln. (Raiko 2020)***

| Parameter | Unit | Biomass boiler | Lime kiln |
|---|---|---|---|
| Gas flow | kg/s | 50 | 25 |
| $N_2$ | wt-% | 62 | 52 |
| $CO_2$ | wt-% | 10 | 20 |
| $H_2O$ | wt-% | 25 | 25 |
| $O_2$ | wt-% | 3 | 3 |

Flue gas from the combustion process consists mainly of nitrogen, carbon dioxide, moisture and air pollutants. The primary pollutants from biomass combustion are particulate matter (PM), carbon monoxide (CO) and hydrocarbons, oxides of nitrogen ($NO_x$) and oxides of sulfur ($SO_x$). Additionally, raw materials, which contain a large fraction of chlorine or other halogens, such as straws and grasses, form acidic gases such as hydrogen chloride (HCl). Acidic gases are corrosive to the boiler, but also highly corrosive air pollutants. (Rosendahl 2013; Ek et al. 2009, p. 380) In the case of a pulp mill, the main impurities are HCl and sulfur oxide ($SO_2$) from the biomass boiler and $SO_2$ from the lime kiln, respectively. However, the content of those in the flue gas is some ppm:s. (Raiko 2020)

Technologies to reduce these air emissions include electrostatic precipitators (ESP), bag filters and wet and dry scrubbers. However, in the case of carbon capturing, the requirements of the flue gas composition depend on the selected process. For example, in the absorption processes the main requirement for the input gas stream is a low

temperature, because according to the Henry's law it increases the solubility of gas in the absorption solvent. Therefore, the flue gas stream must cool down and if it is done with a scrubber, the stream is at the same time washed from the harmful impurities. Some $NO_x$ compounds may still occur, but the effect of those on the carbon capture process operation depends on the selected process. (Raiko 2020)

# 3. POST-COMBUSTION CARBON CAPTURE

Carbon capture is a process where gaseous $CO_2$ is separated from point sources, such as industrial flue gases, or directly from air. Generally, $CO_2$ capture technologies can be divided into pre-, post- or oxy-combustion processes. One significant difference between those technologies is that pre-combustion and oxy-combustion methods are more complex processes and thus it is reasonable to apply those only in new plants, while post-combustion processes can easily be applied to existing plants. (Aghaie et al. 2018) Here, the focus is on capturing $CO_2$ from (biobased) flue gases and therefore only post-combustion technologies are considered. Typically, carbon capture technologies are investigated in fossil fuel power plants, but it is expected that similar technologies can be utilized with bioplants the major difference being the plant size. Bioplants are often smaller in comparison with the conventional ones. (Olsson et al. 2020)

The main challenges of post-combustion carbon capture (PCC) are a relatively low $CO_2$ concentration (typically 10-20 %) and a low pressure. Thus, a driving force for $CO_2$ separation, such as partial pressure, is low and the volume of flue gas to be treated is large. (Zhang et al. 2019) Post-combustion technologies can be categorized (Figure 2) into several main subcategories utilizing absorption, adsorption, cryogenic, membrane and microbial or algal techniques.

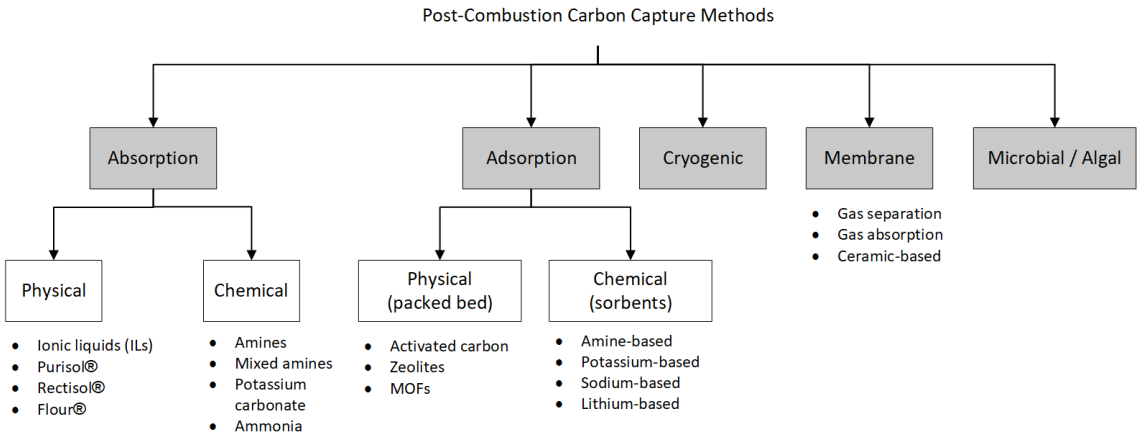



***Figure 2. Classification of post-combustion carbon capture methods (adapted from Aghaie et al. 2018).***

Compared with the other technologies mentioned, chemical absorption is widely used for $CO_2$ capture in the chemical and oil industries, and currently the amine-based chemical absorption process is the industrial benchmark for the post-combustion carbon capturing. Actually, amine absorption is currently the only commercially used PCC

technology since other technologies are still under development. (Karaszova et al. 2020) According to Zhang (2019), Electric Power Research Institute reviewed 125 PCC technologies that are currently in different stages of development, from conceptual analysis (Technology Readiness Level 1) to commercial deployment (TRL9). Among these technologies, 43 % were based on absorption, 23 % on adsorption and 14 % on membranes. Only four absorption projects were at the sub- or full-scale demonstration stage (TRL > 6), while most of the projects reviewed were still on laboratory-, bench- or small pilot-scale (TRL < 5). (Zhang et al. 2019)

Even though the amine absorption is currently ahead in the competition, it is expensive in terms of both capital and operating costs. It is not uncommon that the plants using amine absorption struggle with the economic sustainability of the process. (Karaszova et al. 2020) Therefore, more efficient carbon capturing alternatives are welcomed. In comparison of different capture methods, the most essential issues are the applicability to a power plant or a pulp mill and of course, the price. The used construction materials depend on the corrosiveness of the used solvents and the flue gas impurities and they have a significant effect on the costs, while with successful process design it is possible to develop a process with lower energy consumption. Therefore, materials, solvents as well as process design are currently the most important research topics, because they define the efficiency of the capturing process.

In the following chapters, four technologies for post-combustion carbon capturing are described. Since amines has been used for over 60 years, the mechanism and the involved thermodynamics of the chemical absorption are well-known and the development of new solvents is easier compared with other not so well-known methods. (Aaron & Tsouris 2005) Therefore, the chemical absorption technologies are currently the most available and effective approach for PCC and thus it is the first technology category and discussed widely (Zhang et al. 2019). The other technologies include adsorption with solid sorbents, membrane separation and cryogenic distillation, and those are described more briefly.

## 3.1 Chemical absorption

Absorption is a process in which atoms or molecules enter some bulk phase, either liquid or solid material. Absorption can be physical or chemical, but in carbon capture from flue gases, chemical absorption is preferred due to higher absorption capacity at low $CO_2$ partial pressure. (Sreedhar et al. 2017) The separation process of $CO_2$ with absorption can be done with a liquid solvent or solid matrix, from which a liquid solvent is favoured. Generally, a solvent's chemical affinity with a solute to preferably dissolve on species

over another is utilized. In the $CO_2$ capturing process, the solvent is selected on the basis that it dissolves only $CO_2$, but not any other components, such as oxygen or nitrogen gas, from the flue gas stream. (Aaron & Tsouris 2005) However, the selection of suitable solvent is discussed later in this chapter.

The separation process consists of two stages, which are absorption and desorption. In absorption, chemical solvent is used to dissolve $CO_2$, while in desorption $CO_2$ is recovered from the solvent. (Surampalli et al. 2015) Optimal conditions for absorption are low temperature and high pressure and thus flue gasses need to be cooled before absorption (Kuparinen et al. 2019). The cooling both increases the absorption capacity of the solvent and reduces solvent losses due to the evaporation. Additionally, the flue gases have to be treated to retain acid gases such as $NO_x$ and $SO_2$, which can affect the performance of the capturing process by forming stable salts, and dust particles, which may reduce the efficiency by forming foam in the unit. Also, the oxygen concentration of the treated flue gas must be as low as possible to avoid the corrosion of the equipment. (Sanchez 2016) Figure 3 presents a general flowsheet of the absorption process for the $CO_2$ capture.

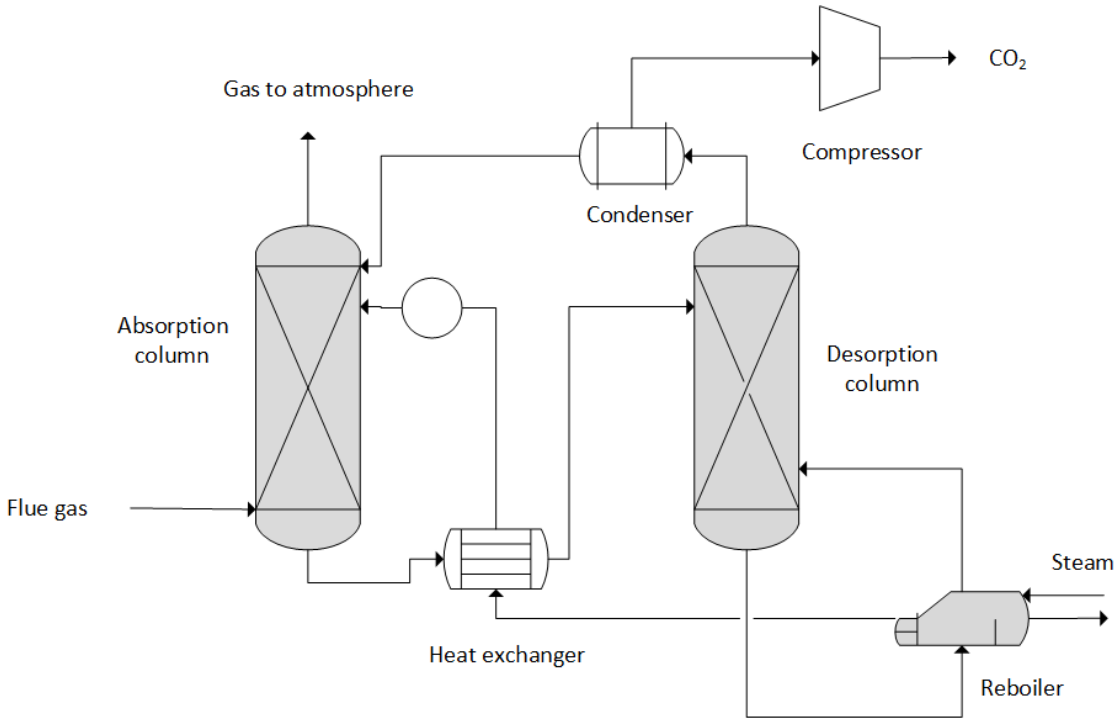



***Figure 3. General flowsheet of absorption process for $CO_2$ capture (adapted from Russo et al. 2013).***

In the first stage, flue gas containing mainly $CO_2$ and inert gases (nitrogen, $N_2$) is transferred to the absorption solvent chamber, where $CO_2$ is separated from the inert gases. The inert gases just bubble out from the solvent chamber, while the $CO_2$ rich

solvent is pumped to the desorption chamber. In desorption chamber $CO_2$ is recovered from the solvent by increasing the temperature or changing the pressure. As opposite to absorption, optimal conditions for desorption and regeneration of the solvent are low pressure and high temperature. After that, the stripped solvent is pumped back to the absorber chamber, where it is ready for a new batch of flue gas. (Surampalli et al. 2015; Aaron & Tsouris 2005) The liberated $CO_2$ is treated in a flash chamber to remove any water or other contaminants. Afterwards the clean $CO_2$ stream is collected for sequestration or further utilization. (Aaron & Tsouris 2005)

Generally, the greatest advantage of chemical absorption is the easy regeneration of solvents while the major drawbacks include less $CO_2$ loading capacity, elevated equipment size, corrosion rate and energy penalties during solvent regeneration step. Some of these could be resolved by improvement in operations involved in the process. For example, the energy penalties can be minimized by maximising the surface area and mass transfer for the process steps. Different absorber configurations employed are packed bed, bubble column, spray column, rotating packed bed and tray towers. Additionally, use of multiple columns, vapor recompression and heat integration in stripping section are some retrofit options that can be used to improve the efficiency. (Sreedhar et al. 2017)

However, the most significant factor in the process is the selection of the solvent. The desired properties for the ideal solvent are high reactivity and absorption capacity with $CO_2$, high stability under extensive thermal and continuous chemical exposure, low vapor pressure, easy regenerability, low environmental impact and low acquisition and production cost. (Sreedhar et al. 2017; Sanchez 2016) Figure 4 presents some absorbents used in carbon capture.

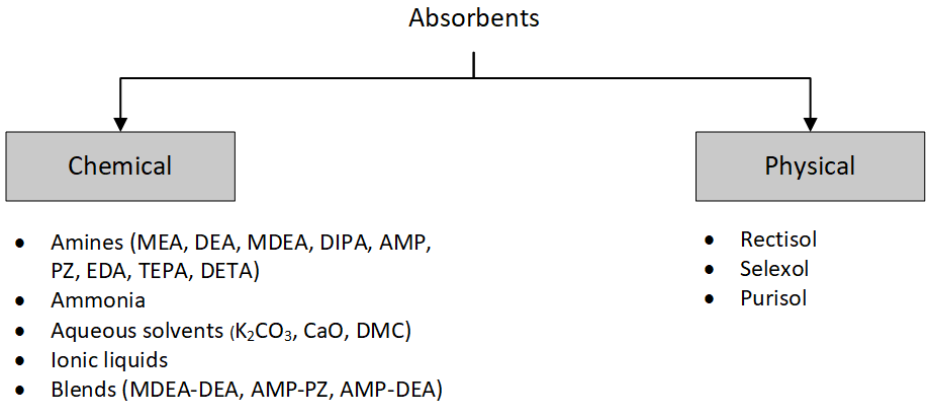


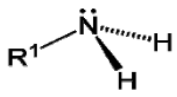
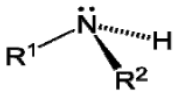
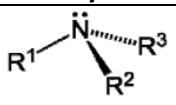

***Figure 4. Types of absorbents employed in carbon capture (adapted from Sreedhar et al. 2017).***

As mentioned before, in the PCC applications chemical absorption is favoured and the used solvents are typically amine-based. However, due to the inherent properties, such as high volatility and corrosiveness, of amines and especially MEA, several research studies have been conducted to replace them with superior solvents. For example, ionic liquids as a physical carbon capture absorption method could have lower volatility, better thermal stability, lower corrosive characteristic, lower degradation rate and lower regeneration cost compared with amines. (Aghaie et al. 2018) Also, aqueous ammonia is investigated to have potential for high $CO_2$ absorption capacity, no degradation, tolerance to oxygen in the flue gas, cost economics, and potential for regeneration using pressure swing. However, literature and breakthroughs in these alternatives are scarce despite having a number of advantages. (Surampalli et al. 2015) Therefore, in the following chapters only two types of solvents are discussed: first the group of amines and after that potassium carbonate which is an aqueous solvent. Both of these have already been applied in industrial scale operation.

### 3.1.1 Amines

In general, amines have been found to have appropriate properties for the absorption process. They are organic compounds that have been used for decades to treat gases from industrial processes and especially alkanolamines are a widely used group of solvents (Sanchez 2016). They are preferred due to their high reactivity with $CO_2$ molecules, high thermal stability, and high absorption capacity (Aghaie et al. 2018). The amines contain an amino group ($-NH_2$) linked by a hydrocarbon radical in their molecule. They can be divided into primary, secondary and tertiary amines depending on the number of hydrogen atoms substituted. (Sanchez 2016) Table 2 presents different groups of amines.

***Table 2. Classification of amines (adapted from Sanchez 2016).***

| **Primary amine** | **Secondary amine** | **Tertiary amine** |
|---|---|---|
|  |  |  |
| **Amine** | **Chemical formula** | **Classification** |
| Monoethanolamine (MEA) | $C_2H_4OH\text{-}NH_2$ | Primary |
| Diglycolamine (DGA) | $HOC_2H_4OC_2H_4\text{-}NH_2$ | Primary |
| Diethanolamine (DEA) | $C_2H_4OH\text{-}NH\text{-}C_2H_4OH$ | Secondary |
| Diisopropanolamine (DIPA) | $C_3H_5OH\text{-}NH\text{-}C_3H_5OH$ | Secondary |
| Triethanolamine (TEA) | $C_2H_4OH\text{-}NH\text{-}C_2H_4OH$ | Tertiary |
| Methyldiethanolamine (MDEA) | $(HO\text{-}CH_2CH_2)_2\text{-}N\text{-}CH_3$ | Tertiary |

Primary amines contain an ammonia molecule from which a single hydrogen atom is replaced. Monoetanolamine (MEA) and diglycolamine (DGA) are examples of primary amines. The reactivity of those amines with acid gases is very good and a separation is easy, but the absorption capacity is relatively low, since two moles of amines is required to the absorption of one mole of $CO_2$. Additionally, the reaction between the $CO_2$ and the amine is very stable meaning that high amount of energy is needed for the regeneration. (Sanchez 2016)

Among all amine groups, MEA is widely used as a reference solvent in the process. The advantages of MEA include low cost, thermal stability, partial removal of carbonyl sulfide (COS) and high reactivity. (Sanchez 2016) However, application of MEA has several disadvantages including low absorption capacity for $CO_2$ requiring large volumes and large equipment size, high equipment corrosion rate, and amine degradation by $SO_2$, $NO_2$ (nitrogen dioxide) and $O_2$ in the flue gases which causes high energy consumption. (Aghaie et al. 2018, Surampalli et al. 2015) MEA is also more volatile than diethanolamine (DEA). (Sanchez 2016) These properties cause high energy demand and greater losses of the solvent meaning high costs and additionally environmental issues due to the volatility. Therefore, the main challenges of the absorption process using MEA are the optimization of solvent regeneration and energy consumption and minimizing the oxygen and acidic gas content of the flue gas causing corrosion and solvent loss and high regeneration cost. (Aaron & Tsouris 2005)

Since secondary and tertiary amines have more substituted nitrogen atoms, they have different chemical properties and are therefore investigated as a replacement for MEA. Secondary amines, such as diethanolamine (DEA) and diisopropanolamine (DIPA) are less reactive than primary amines and have a lower degree of degradation in the presence of COS and $CS_2$ (carbon disulfide). Tertiary amines, such as methyldiethanolamine (MDEA) and triethanolamine (TEA) are less reactive than secondary amines and have a greater absorption capacity. Generally, higher-degree amines require less energy to regenerate the solvent and due to the higher absorption capacity, the amount of the solution needed is lower. However, the reaction rate of tertiary and secondary amines is lower than primary amines meaning slower reactions and thus the required dimensions of the plant are greater. Additionally, viscosity limits the concentration in which a solvent can be used. (Sanchez 2016) It is possible to mix secondary or tertiary amines with primary amines to achieve a solvent with better properties, but probably there remain still disadvantages such as strong corrosion and high energy requirement for regeneration (Borhani et al. 2015).

### 3.1.2 Potassium carbonate mediated by carbonic anhydrase

Potassium carbonate ($K_2CO_3$, PC) process is an important technology to reduce $CO_2$ emissions and it was originally developed for the synthesis of liquid fuel from coal. It has been applied globally in more than 600 plants for $CO_2$ and hydrogen sulfide removal from ammonia synthesis gas, crude hydrogen, natural gas and town gas, for instance. (Borhani et al. 2015) Recently, the research has been more focused on utilizing the PC process in carbon capturing from flue gases. (Hu et al. 2016)

The absorption between $CO_2$ and PC solution is an exothermic reaction during which the potassium carbonate is transformed into potassium bicarbonate ($KHCO_3$) according to the following chemical equation:

$$CO_2 + H_2O + K_2CO_3 \rightleftharpoons 2\,KHCO_3. \quad (3)$$

In commercial operations, the pH range of interest is at pH higher than 8. Under these conditions, the principal mechanism is based on the formation of bicarbonate ($HCO_3^-$) through the reaction of $CO_2$ with hydroxide ($OH^-$) and the reaction of $HCO_3^-$ with $OH^-$. (Borhani et al. 2015)

The main advantages of carbonate solutions in carbon capture applications are high chemical solubility of $CO_2$ in the carbonate/bicarbonate system, easy regeneration, low solvent cost, low toxicity of solvent and low tendency to degradation. One of the main advantages compared with amine solvents is the easy regeneration of the solvent due to the chemical properties of potassium carbonate and high operating pressure. In the PC process, $CO_2$ is absorbed at nearly the same temperature as it is desorbed and therefore savings in energy consumption are achieved. (Hu et al. 2016; Borhani et al. 2015)

However, each process has also limitations. The main disadvantages of the PC solutions used in carbon capture applications are the slow reaction rate and low mass transfer in the liquid phase and the precipitation of the solvent in the fouling and accumulation of crystals in the reboilers and pipeline of the process. Additionally, PC solution is corrosive to the carbon steel, but still less corrosive than amines. (Borhani et al. 2015) From these limitations, the biggest weakness of the process is the firstly mentioned slow reaction rate, which leads to the requirement of larger equipment and thus high capital investment and operation penalty (Hu et al. 2016). However, the issue can be improved by using some promoter in the PC solutions. The promoters of PC solution are usually either organic or inorganic promoters or biological enzymes. (Borhani et al. 2015) Many chemical catalysts, such as arsenite, sulfide, hypochloride and formaldehyde, have been studied in this mean. Most of them can accelerate the $CO_2$ absorption rate by 2-5 times,

but at the same time they have drawbacks such as toxicity and instability or corrosiveness. (Ye & Lu 2014) Therefore, one promising alternative is carbonic anhydrase.

Carbonic anhydrase (CA) is an enzyme found in all organisms since it plays a role in $CO_2$ metabolism. It belongs to a group of zinc metalloenzymes. (Bhatia et al. 2019) Since the use of CA is considered environmentally friendly, an efficient catalyst for $CO_2$ hydration and has little influence on the heat of absorption, it has been researched as a promoter in PC solutions but also in amine solutions and in attached to membranes (Hu et al. 2016).

By using CA in the PC solutions, it is possible to increase the $CO_2$ absorption by 6-20 fold. However, as biological catalysts, enzymes are typically adjusted to survive in mild conditions and thus in harsh industrial conditions, the high temperatures and high pH can lead to enzyme denaturation and the decreased performance of the promoter. (Hu et al. 2016) Additionally, high enzyme cost and scaling up the enzyme production process from laboratory-scale to large-scale industrial process may cause challenges (Surampalli et al. 2015). However, some of the issues can be avoided with the immobilization of the enzyme or by developing or finding thermally stable enzyme variants (Hu et al. 2016). According to Wu et al. (2020), the strategies for improving the thermostability of CA variants include, for example, increasing surface loop rigidity and surface compactness, decreasing surface hydrophobicity and introducing conserved disulfide bridge. Alvizo et al. (2014) reported the enhanced properties of CA from *Desulfovibrio vulgaris* using directed evolution, for instance. The found CA variants were able to tolerate temperatures of up to 107 °C and pH > 10, which led to the $CO_2$ absorption rate of 25 fold compared with the noncatalyzed reaction.

## 3.2 Adsorption with solid sorbents

Adsorption with solid sorbents is a process, where solid materials are used to interact with $CO_2$ to form stable compounds under certain conditions. After that, under changed conditions, the adsorbent releases the $CO_2$ molecules and re-form the original compound. Thus, adsorption, as well as absorption, is a two-step process, where the $CO_2$ molecules are first captured from the gas mixture and after that released from the sorbent or solvent by changing process conditions, usually temperature or pressure. In $CO_2$ capture processes, the used adsorbents are active granulated carbon, alumina and metal oxides and zeolites, for instance. (Sanchez 2016, p. 17; Rackley 2010)

Just like absorption, adsorption can also be either chemical or physical. In chemical adsorption, the molecules are linked to the sorbent with chemical bonds, whereas physical adsorption is based on intermolecular forces between the gas molecules and the surface of the sorbent. (Rackley 2010) The adsorption method depends on the process temperature. Typically, physical adsorption occurs when low temperature sorbents are used while the high temperature sorbents form chemical bonds with $CO_2$. In the flue gas treatment, the more common adsorption method is physical adsorption because the temperature is usually quite low, less than 100 °C. (Hedin et al. 2013)

Even though the separation process in adsorption differs from absorption, the chemical and physical bonds can be similar. However, in adsorption, the adsorbed molecules, here $CO_2$, remain on the surface of the sorbent while in absorption processes the molecules enter into the solvent to form a solution. (Rackley 2010) Since adsorption occurs on the surface of the adsorbent, the most important characteristic of it is the quantity of sorbate that a given quantity of adsorbent can hold under certain operating conditions. To maximize the working capacity, the surface area of the sorbent must also be maximized. However, it is important that the sorbent is selective for $CO_2$ but not for other gases to ensure the purity of the end product. (Hedin et al. 2013)

Since the uptake of gas to the sorbent depends on both pressure and temperature, the developed adsorption processes for $CO_2$ capture are based on changes in pressure or temperature. In temperature swing adsorption (TSA), the regeneration of the adsorbent is done by raising the temperature, whereas in pressure swing adsorption (PSA), elevated pressures are used. From these alternatives, PSA seems to be superior to TSA due to its lower energy consumption and higher regeneration rate (Aaron & Tsouris 2005).

One of the main advantages of adsorption is that the vessels need to withstand small pressure changes, but not significant temperature changes or corrosive solutions like in cryogenic separation or liquid absorption. (Aaron & Tsouris 2005) However, the system cannot easily handle streams that have high concentration of $CO_2$. Flue gases typically have $CO_2$ concentration of 10-20 %, while the suitable concentration for the process is usually 0.04-1.5 %. Additionally, the currently available sorbents are not selective enough for separation of $CO_2$ from flue gases. Thus, the process is less efficient, and the separated $CO_2$ stream includes impurities such as $N_2$. (Surampalli et al. 2015) However, adsorption would have a satisfactory role in a hybrid system. Since the system can handle only low concentration of $CO_2$, it could be placed after another separation process.

## 3.3 Membrane separation

The capture and separation of $CO_2$ can also be performed with selective membranes. Membrane separation processes are based on the membranes acting as an interface between solvent (liquid phase) and flue gases containing $CO_2$ (gaseous phase). (Sanchez 2016) The basic principle is that the desired constituents of the gas permeate through the porous structure of solid membrane materials, while the undesired constituents are not able to permeate the membrane. In PCC applications, $CO_2$ is let through the membrane and the other compounds of the flue gas are blocked. (Surampalli et al. 2015) Figure 5 presents the basic principle of membrane separation technologies.

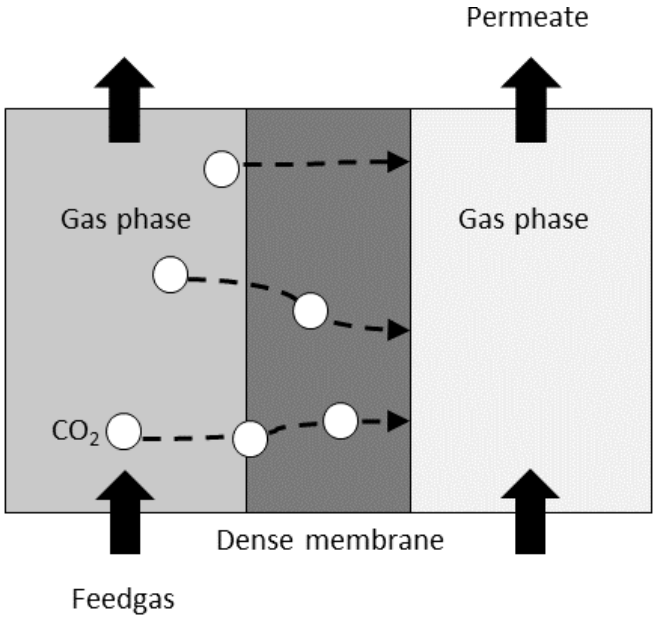



***Figure 5. Schematic of membrane gas separation in $CO_2$ capturing (adapted from Siagian et al. 2019).***

The degree of the selectivity of membranes to different gases depends on the construction material. In $CO_2$ capture systems, possible alternatives are typically polymeric, metallic and ceramic materials. (Surampalli et al. 2015) The advantages of the membrane separation are low energy consumption, low operational costs, small footprint and easy scale-up. Membranes are waste-free and also easy to incorporate into existing technologies. (Karaszova et al. 2020)

The major disadvantage of the membrane separation is that carbon dioxide is permitted to be transported through membrane only in conditions that the pressure on both sides of the membrane, in the liquid and gaseous phase, is equal. The effectiveness of the process depends on both the partial pressure and concentration of $CO_2$ in the gas flow. The concentration of $CO_2$ of the gas flow should be over 20 % to make the membrane separation process recommended method. Since the $CO_2$ concentration in flue gases is

typically 10-20 % and the pressure of the gas flow is low, membrane separation is not usually used in post-combustion carbon capturing. (Sanchez 2016) Additionally, the carbon dioxide purity in the separated gas is typically low, because the selectivity of the separation process is low. This can be avoided with multilayer process, but it increases the capital and maintenance costs. (Sanchez 2016; Surampalli et al. 2015)

Currently, membrane technologies have successfully been applied in applications such as natural gas or biogas purification and removal of heavy metals from water. However, there is still a gap between membrane separation studies and commercial applications in post-combustion $CO_2$ capture. Thus, open questions, such as the long-term stability of the membrane materials, must be solved first before wider spread. (Karaszova et al. 2020)

## 3.4 Cryogenic distillation

In cryogenic carbon removal methods, carbon is captured from flue gases in a liquid form. The process consists of a series of compression, cooling and expansion steps, during which the temperature and pressure are lowered and increased aiming to liquefy $CO_2$. Under the right conditions, $CO_2$ condenses, while the rest of the gas mixture remains in gaseous form and can be released through an outlet at the top of the chamber. Then, the liquid $CO_2$ can be collected at the bottom of the chamber. (Surampalli et al. 2015; Aaron & Tsouris 2005)

If the $CO_2$ feed is properly conditioned, the main advantage of cryogenic process is the higher recovery of $CO_2$. The purity of the $CO_2$ after distillation can be 99.95 %. Additionally, the product of the process is liquid $CO_2$, which is ready for transport. (Aaron & Tsouris 2005) However, contaminants, such as SOx and NOx, may hinder the efficiency and the need for pressurization and refrigeration make cryogenic processes extremely energy intensive and expensive. Thus, cryogenic separation is preferred for the purification of $CO_2$ from streams with high $CO_2$ concentrations (typically > 90 %). Therefore, it is not the preferred method for dilute flue gases from biomass combustion. (Surampalli et al. 2015)

# 4. CARBON UTILIZATION

After the capturing, there are several options for the $CO_2$ processing. The captured $CO_2$ can be stored (CCS) in an underground geological formation or it can be utilized (CCU) through numerous pathways. In this thesis, the focus is on utilization technologies and therefore only CCU methods are considered. One classification for the main $CO_2$ utilization routes is presented in Figure 6.

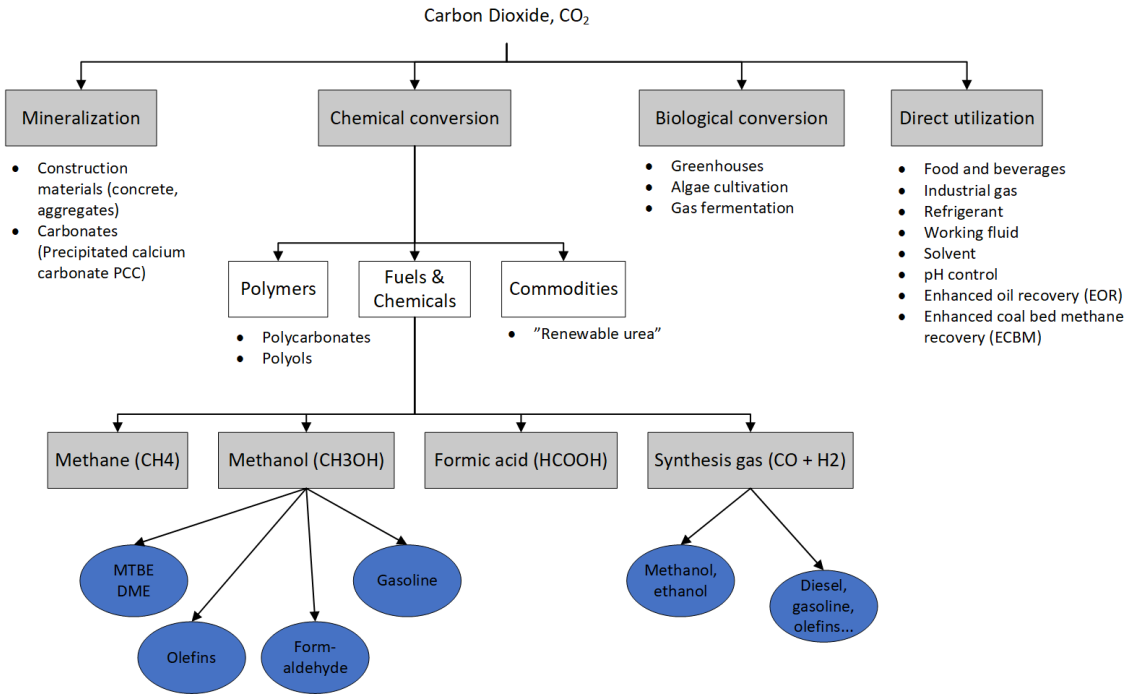



***Figure 6. Main $CO_2$ utilization routes and applications. MTBE means methyl-tert-butylether and DME is dimethylether. (Adapted from VTT a)***

The utilization routes are usually divided into chemical and biological conversion, mineralization and direct utilization meaning that the captured $CO_2$ can be utilized as a building block or feedstock for the production of chemicals or fuels or it can be used directly as it is. (Chauvy et al. 2019) The chemical and biological conversion routes use, for example, thermocatalytic, electrochemical, biochemical and photocatalytic conversion techniques (Zhang et al. 2020). Here, the main focus is on conversion technologies, while direct utilization and mineralization technologies are discussed only briefly.

The synthetization of other products from $CO_2$ is not a new idea, it is already commercialized in industrial processes which derive $CO_2$ as a by-product, for example the production of hydrogen ($H_2$) by the steam reforming of natural gas or ethanol production by fermentation. However, the value chain for captured $CO_2$ from flue gas

streams is similar to the conventional one that already exists for the $CO_2$ by-product. If the obtained $CO_2$ is not utilized directly in the plant, it is liquefied and then transported to end users in a liquid form. (Pérez-Forter et al. 2016)

In the ambient conditions, $CO_2$ is a colourless and odourless gas. It is a linear molecule with a double bond between the carbon and oxygen atoms (O=C=O) and due to the double bonds, the molecule is highly stable. Thus, a substantial input of energy, effective reaction conditions, and often active catalysts are required for the conversion process. (Song 2006) In the CCU processes, it is important to consider where the used energy or electricity is coming from. It is not sensible to capture $CO_2$ from flue gases to control the emissions and then convert it with fossil energy emitting more $CO_2$ into the atmosphere. Therefore, one of the keys to future developments is the production of efficient and cheap catalysts to decrease the energy consumption of the conversion processes (Zhang et al. 2020). Additionally, in many conversion processes $CO_2$ is combined with $H_2$, which is conventionally produced from fossil fuels by the steam reforming of natural gas or coal gasification. Thus, to reduce the life cycle $CO_2$ emissions of the CCU process, the used $H_2$ must be produced in a carbon-free way, such as by water electrolysis using renewable electricity or by biomass gasification. (Pérez-Fortes et al. 2016) However, currently one of the main economic challenges of CCU applications is particularly the high cost of low-carbon hydrogen. (Onarheim et al. 2015)

Currently, there are $CO_2$ utilization systems of two kind. Urea, formic acid, methanol, cyclic carbonates and salicylic acid are common products that are conventionally made from $CO_2$. At the moment, the used $CO_2$ is seldom from carbon capturing, but it can be expected that if the carbon capturing processes spread, it does not matter, where the raw material $CO_2$ originates. The second group include products, that are conventionally made from some other raw materials and are now under development to utilize $CO_2$. The latter pathways are in varying levels of development ranging from the laboratory to the demonstration and pilot-scale. (Zhang et al. 2020; Chauvy et al. 2019) Some main $CO_2$-based products are categorized by the technology readiness levels (TRL) and presented in Figure 7. Since some of the listed products can be produced via multiple processes, the presented TRL is the highest one for each conversion pathway. As can be noted, there are numerous products but only a few are already commercialized.

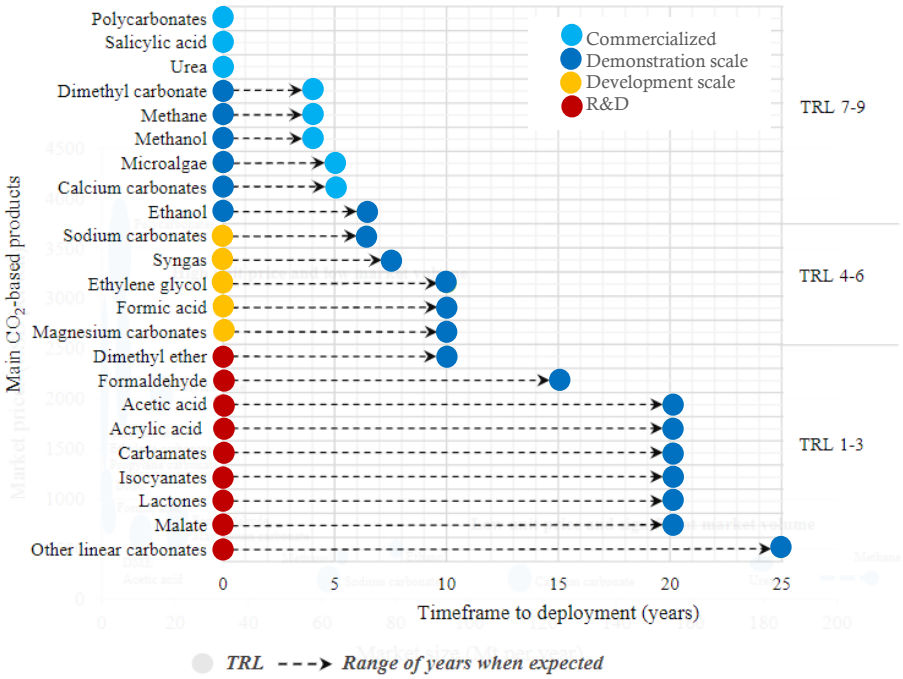



***Figure 7. $CO_2$-based products categorized by technology readiness levels (adapted from Chauvy et al. 2019).***

Ideally, the CCU system is a process, which needs low additional energy, has simple reaction mechanisms and produces end-product that has high future market size and value. Unfortunately, $CO_2$-based products, just like almost all products, are either high added value products with low market volume or low added value products that have a significant market. Both high added value and high market volume cannot be achieved simultaneously. (Chauvy et al. 2019; Onarheim et al. 2015) Figure 8 presents this visually. As can be seen from the figure, urea and methane are examples of the products with a large market capacity and low price, while polycarbonates and polyurethane are high added value products with a low market volume. However, in addition to the current market size, political decisions can have a significant effect on the future market potential, especially in the case of $CO_2$ derived fuels, such as methanol and dimethyl ether (DME). Suitable tax decisions may change an unprofitable process to a feasible one in the future.

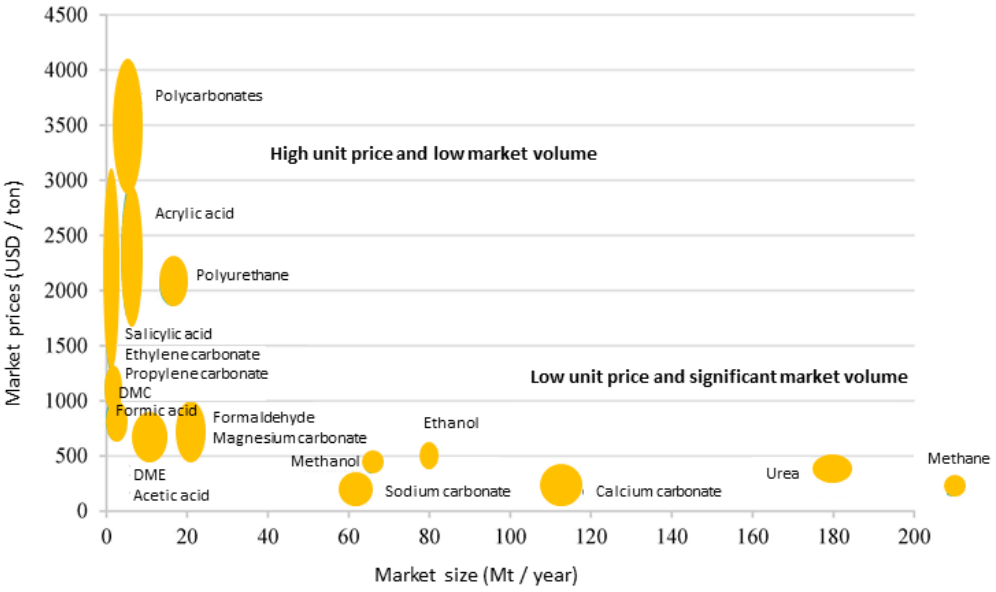



***Figure 8. $CO_2$-based compounds categorized by market sizes and market prices (adapted from Chauvy et al. 2019).***

In the following chapters, three $CO_2$ conversion technologies are described. Bioethanol production by gas fermentation is an example of a biological conversion process while methanol hydrogenation and polyol copolymerization are examples of the chemical conversion processes. Lastly, a few other promising technologies are presented briefly. Ethanol, methanol and polyols have been chosen for the examined end-products since they all are basic buildings blocks in chemical industry and have numerous applications. Also, ethanol and methanol have potential in fuel applications. Since, the techno-economic analysis of this thesis is a bioethanol production process, it is described in more detail here.

## 4.1 Bioethanol from syngas fermentation

Ethanol ($C_2H_5OH$, EtOH) is simple alcohol, which has numerous uses. The largest single use of ethanol is as an alternative fuel source or fuel additive. For example, hydrous ethanol containing about 95 % ethanol and 5 % water can be used as fuel in new gasoline fueled cars, which are common in countries such as Brazil. However, in addition to the use as a fuel, ethanol is one of the largest volume organic chemicals used as an industrial ingredient in the production of paints, markers, polishes, plastics and cosmetics. Typically, in industrial applications the used ethanol is anhydrous (> 99.5 wt-%). Due to its low boiling point and suitable molecular structure, ethanol is also commonly used as a solvent, because it is easy to remove from a solution and it allows for the dissolving of hydrophobic, hydrophilic, polar and nonpolar compounds. (Bayens et al. 2015) Approximately 15 % of the total global ethanol consumption is for non-fuel applications.

In 2016, the global demand of industrial grade ethanol was 20 billion litres and the production capacity is expected to continue growing in the future. (Beroe)

Ethanol can be produced from petroleum-based feedstocks or from renewable biomass, in which case it is called bioethanol. Approximately 9 % of the world production of ethanol is produced synthetically from ethene, while the remaining 91 % is produced using biochemical pathways. (Soccol et al. 2016) Principally, ethanol is produced biochemically via fermentation of biomass, such as sugarcane or corn, and is called first generation bioethanol. In the traditional pathway, biomass is pretreated with hydrolyzation and then the released sugars are fermented to bioethanol by the action of microorganisms, which are usually yeast. (Bayens et al. 2015) However, apart from liquid substrates, it is also possible to use gaseous compounds, namely syngas, as a raw material for fermentation.

In gas fermentation, anaerobic bacteria metabolize syngas containing CO, $H_2$ and $CO_2$ into cell mass, acids (e.g. acetate) and solvents (e.g. ethanol). The possible origins for the gas substrate are, for instance,

1) syngas from gasification of lignocellulosic biomass or municipal solid waste
2) exhaust gas from steel production and cement industries
3) captured $CO_2$ blended with $H_2$
4) reformed biogas.

Since the gas fermentation offers versatile waste-to-fuel or circular economy routes, it has gained attention as a promising ethanol production method. Currently, there are at least three commercial-scale gas fermentation ethanol plants under construction or have started operation. Additionally, many pilot plants have been in operation for long periods of time. (Medeiros et al. 2019)

In the case of carbon capture and utilization, it would be possible to ferment the captured $CO_2$ directly to ethanol in the presence of renewable $H_2$. However, the process is more efficient if the feedstock contains both $CO_2$ and CO. Thus, it is reasonable to first convert the captured $CO_2$ and $H_2$ to syngas via reverse water gas shift (RWGS) reaction and then ferment the produced syngas. Biochemically, the overall stoichiometry for the conversion of CO, $CO_2$ and $H_2$ to ethanol can be presented by the following Equations:

$$6\,CO + 3\,H_2O \rightarrow C_2H_5OH + 4\,CO_2 \quad (4)$$

$$2\,CO_2 + 6\,H_2 \rightarrow C_2H_5OH + 3\,H_2O \quad (5)$$

$$4\,CO + 2\,H_2O \rightarrow CH_3COOH + 2\,CO_2 \quad (6)$$

$$2\,CO_2 + 4\,H_2 \rightarrow CH_3COOH + 2\,H_2O. \quad (7)$$

Equations 4 and 5 present the formation of ethanol from CO and $CO_2$ while Equations 6 and 7 stand for the production of acetic acid ($CH_3COOH$) from the same substrates. In the case of ethanol production, acetic acid is not a desired product, but the formation of it cannot be totally prevented. (Amarasekara 2013). In Equations 4 and 6, CO is the sole carbon and energy source, while in Equations 5 and 7 $CO_2$ is the carbon source and $H_2$ the energy source (Daniell et al. 2012).

The potential biocatalyst (bacteria) for the syngas fermentation process are for example acetogens *Clostridium ragsdalei, Clostridium autoethanodenum* and *Clostridium ljungdahlii*. These microorganisms use the reductive acetyl CoA pathway, also known as the Wood-Ljungdahl pathway, to ferment syngas to mainly ethanol and acetic acid. (Daniell et al. 2012) Acetyl CoA pathway is an irreversible, non-cyclic pathway, which takes place under strictly anaerobic conditions. It is presented in Figure 9. The pathway consists of two branches, from which the left one is known as the methyl branch, whereas the right branch as the carbonyl branch. Through these branches $CO_2$ is reduced to CO, which is then converted to acetyl coenzyme (acetyl-CoA) and further to ethanol and acetic acid via several enzyme-dependent reactions which can be seen from the figure. However, one thing that must be noted is the role of acetyl-CoA. It acts both as a precursor for the cell macromolecule and as an energy source in the pathway. (Kennes et al. 2015; Amarasekara 2013) Additionally, the electrons required to run the acetyl CoA pathway are originating from the electron bifurcation, which is a complex mechanism serie during which $H_2$ gas is split up the pair of electrons to obtain enough reduction potential. (Moran 2018)

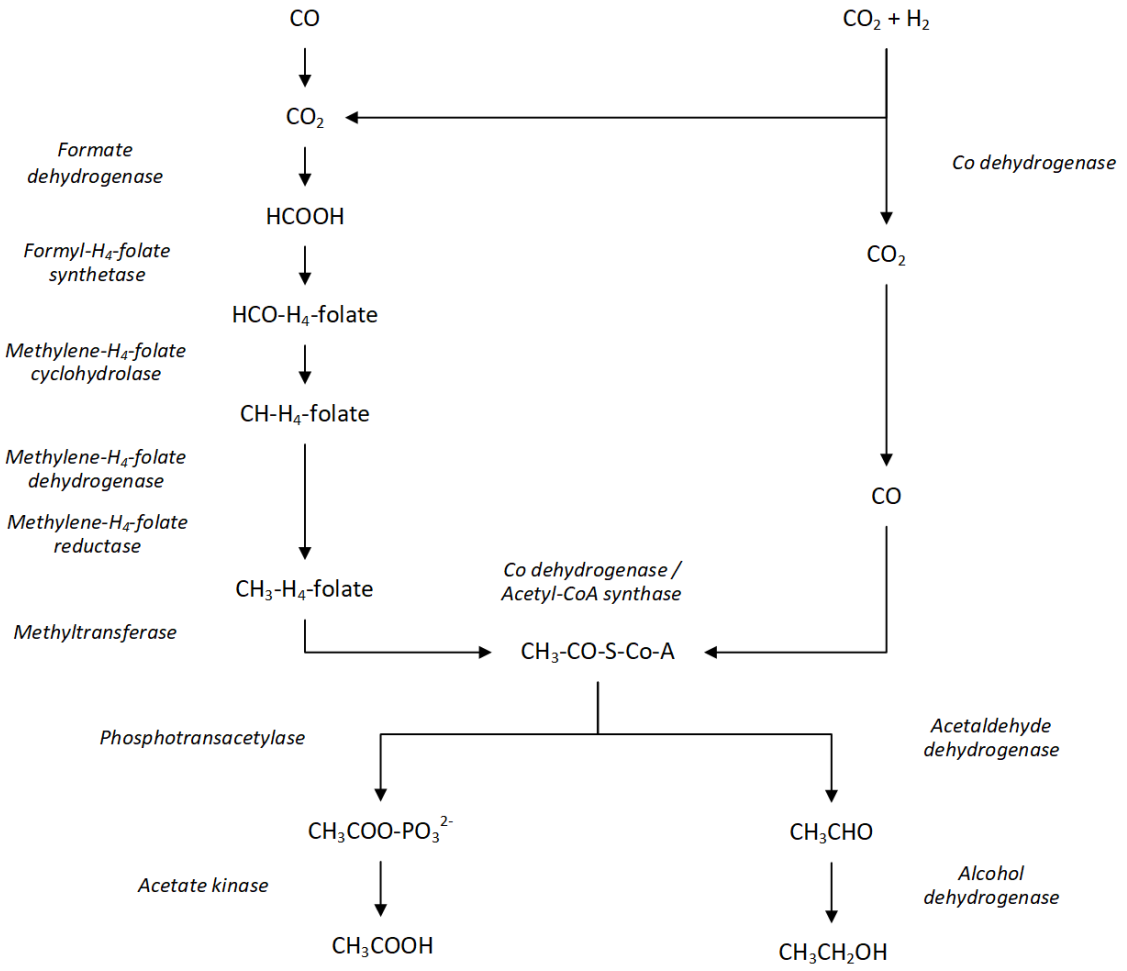



***Figure 9. Simplified scheme of the acetyl-CoA pathway for acetogenic micro-organisms leading to the production of ethanol and acetic acid (adapted from Amarasekara 2013).***

In the methyl branch, $CO_2$ is first reduced to formate ($HCOO^-$) by the formate dehydrogenase enzyme. Then the formate is converted through several intermediate steps and enzymes to 5-methyl-$H_4$-folate and further to $CH_3$-$H_4$-folate, which is transferred to the cobalt center of the iron-sulfur protein to produce the methyl group. In the carbonyl branch, the procedure is simpler compared with the methyl branch: a carbonyl group is first produced and then it is merged with the methyl group to produce acetyl-CoA. The most significant enzyme of the carbonyl branch is carbonyl dehydrogenase, which reduces $CO_2$ to CO as the carbonyl group.

When acetyl-CoA is produced, it can be converted to acetic acid and ethanol. Phosphotransacetylase catalyzes the conversion of acetyl-CoA to the intermediate acetyl-phosphate ($CH_3COO^-PO_3^{2-}$) while acetyl-phosphate is converted to acetate by acetate kinase. Ethanol is produced from acetyl-CoA via acetaldehyde ($CH_3CHO$) intermediate in the presence of acetaldehyde dehydrogenase and alcohol dehydrogenase enzymes. The difference between acetic acid and ethanol formation is

that acetic acid is produced during the growth phase of the microorganism while ethanol is formed during the non-growth phase. Therefore, acetic acid is produced in the presence of ADP and ATP while in the ethanol formation the reducing potential in the form of NADPH is utilized.

The advantages of syngas fermentation using biocatalyst include moderate temperatures and pressures close to atmospheric pressure, which result in energy savings in industrial-scale operations. Additionally, the designs of the reactors are simpler and no high-temperature, pressure-resistant materials are needed in the fabrication of the reactors. Moreover, due to the high enzymatic specificity, high reaction specificity is achieved and due to the operation at ambient temperature, thermodynamic equilibrium relationship is avoided resulting higher conversion efficiencies. Furthermore, biocatalysts are flexible with the impurities and composition ($CO/H_2$ ratio) of syngas. They are known to have such a high tolerance for sulfur-containing gases and also for smaller amounts of chlorine-containing compounds. (Kennes et al. 2015; Amarasekara 2013) Additionally, here the desired product is ethanol, but depending on the used bacteria the various products that can be produced from the gaseous feedstock include 2,3-butanediol, lactic acid, butyric acid and butanol, for instance. (Kennes et al. 2015)

The major disadvantage of syngas fermentation is gas-to-liquid mass transfer limitation due to poor solubility of CO and $H_2$ components of syngas in aqueous broths, which results in low substrate uptake by microbes. It leads to lower conversion efficiencies and thus low ethanol yields. Additionally, the cost of fermentation media and its buffering systems are important factors in a large-scale operation. (Amarasekara 2013) However, the ethanol yield can be maximized by optimization of culture media and nutrient content, pH, inhibitors, gas impurities and gas pressure. Also, the configuration of reactor is closely related to the ethanol yield. The most important parameters for an efficient fermentation bioreactor are high mass transfer rates, high cell densities, low operation and maintenance cost and easy scale-up. Some of the common reactor types for syngas fermentation are continuous stirred tank reactor (CSTR), packed bed reactors and trickle bed reactors. (Amarasekara 2013; Daniell et al. 2012)

After the fermentation, a downstream product separation is required to separate ethanol from the fermentation broth. Syngas fermentation takes place in an aqueous phase and therefore the end product is a mash containing 2-12 wt-% ethanol in water and additionally small amounts of buffering salts and microorganisms. (Amarasekara 2013) The downstream process of the broth of syngas fermentation can be largely carried out in the same manner as for conventional fermentation. However, in gas fermentation the ethanol concentration in the broth is lower and thus more energy is required for the

downstream product recovery compared with conventional fermentation. (Daniell et al. 2012)

Possible separation technologies for the fermentation products are, for example, distillation, liquid-liquid extraction, gas stripping, adsorption and membrane techniques, but each of these technologies has their own benefits and drawbacks (Liew et al. 2016). Although distillation is energy intensive, it is a commonly used and mature method for the separation of lower boiling point products, such as ethanol (Daniell (2012). If the desired product is anhydrous ethanol (> 95.6 wt-%), the separation is done in two steps in order to remove the water from the azeotropic mixture. The first step is a standard distillation, while the second method can be, for example, extractive distillation, azeotropic distillation or molecular sieve system. (Busic et al. 2018) A molecular sieve is a material, usually silicagel, with unifrom size. These pores are small enough to block large molecules and at the same time allow small molecules to pass. (Bayens et al. 2015)

## 4.2 Methanol synthetization

Methanol ($CH_3OH$) is one of the most important bulk chemicals for the chemical industry. It is used as a raw material in producing variety of chemicals, such as formaldehyde, methyl tert-butyl ether and acetic acid. These chemicals are subsequently utilized in the production of paints, resins, adhesives, antifreezes and plastics. Due to excellent combustion characteristics, methanol is also suitable for the use as a fuel directly or for the derivates such as DME. (Artz et al. 2018)

Currently, most of the sold methanol is produced from fossil-based natural gas through steam reforming process or by coal gasification. In the latter process, the coal is first converted to syngas, which contains mostly CO, $CO_2$ and $H_2$, and is then converted to methanol. (Bellotti et al. 2017) The main disadvantage of the conventional methanol production is the amount of emitted $CO_2$: the average $CO_2$ emissions of European conventional methanol plants is estimated 0.76 ton $CO_2$-eq/ton methanol (Meunier et al. 2020). Therefore, as an alternative to the traditional approach, methanol can be produced from the captured $CO_2$. These pathways include direct hydrogenation of $CO_2$ with $H_2$ or $CO_2$ conversion into syngas via RWGS reaction and further hydrogenation of the syngas to methanol. As an alternative, also electrochemically route including $CO_2$ reduction and $H_2O$ oxidation is possible. (Artz et al. 2018; Peréz-Fortes et al. 2016)

The production of methanol on a large scale process is based on the following reactions:

$$CO + 2\,H_2 \leftrightarrow CH_3OH \tag{8}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{9}$$

$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O. \quad (10)$$

Equation 8 stands for methanol synthesis from CO, Equation 9 for the RWGS reaction and Equation 10 for methanol synthesis from $CO_2$. (Meunier et al. 2020) From these routes, the direct hydrogenation of $CO_2$ is more studied since it has only one step and thus it is the most direct route. It is a catalytic reaction taking place in ranges of temperature and pressure of 250-300 °C and 50-100 bar. (Bellotti et al. 2017) However, even though the direct hydrogenation has less reaction steps, it consumes more hydrogen than methanol synthesis from CO. As mentioned before, the used hydrogen has a significant effect on the energy consumption of the process and therefore on the life cycle $CO_2$ emissions and costs of the process. Thus, it is an ongoing research topic whether it is more efficient to synthesize methanol from $CO_2$ or from CO even though the process includes more steps. (Artz et al. 2018)

The main advantages of the methanol production from captured $CO_2$ using renewable energy sources are the decreased level of emitted $CO_2$ and the decreased consumption of fossil resources. However, these decreases are strongly dependent on the used heat and electricity sources and especially the production method of $H_2$. Additionally, despite the benefits of the developed processes, they have challenges with low yields, reaction conditions, selectivity and environmental issues. Therefore, they have not reached the economic feasibility yet. (Meunier et al. 2020)

## 4.3 Polyol copolymerization

The captured $CO_2$ can be used as a raw material in polymer industry. One promising market segment in that field is the copolymerization of $CO_2$ and epoxides in order to produce polyols, which can be further converted, for example, to polyurethanes. Polyurethanes are one of the most commercially important specialty polymers worldwide, because they have numerous applications, for example, in heating systems, automobiles, beddings, furniture, refrigerators and buildings as insulations, coatings and foamed plastics. Usually, they are combined with materials such as wood, metals, other polymers or textiles and therefore the usage of polyurethanes is not always visible in the end product. However, due to their advantages in safety, light weight, durability, comfort and energy savings they have nowadays spread everywhere. (Eling et al. 2020; Langanke et al. 2014)

The main building blocks of polyurethanes are polyols and polyisocyanates. Polyols are organic compounds containing multiple hydroxyl groups. The product of the epoxide and $CO_2$ copolymerization reaction can be either polycarbonate polyol or polyethercarbonate

polyol depending on the reaction conditions and the catalyst. (Langanke et al. 2014) Both polycarbonate polyols and polyethercarbonate polyols can be used in the production of polyurethanes, but they have different properties. Polycarbonate polyols are used in applications, where high hydrolytic, thermal and UV stability are required. These usages include very high-performance applications, for example, in elastomers, coatings and adhesives. Polyether polyols are the most common polyols with 70 % global market share, and they are used in applications where that high-performance is not required. (VTT b)

$CO_2$ utilization in polyol production has been examined in many studies, but usually the focus has been on substituting part of the used epoxide (usually propylene oxide) by $CO_2$ without taking a stand to the origin of the epoxide. In commercially available polyols the $CO_2$ content is limited to 40 %, because with higher $CO_2$ contents the produced polyols exhibit a significantly higher viscosity, which causes problems during the processing. (Eling et al. 2020; Fernández-Dacosta et al. 2017; Langanke et al. 2014) However, VTT (Technical Research Center of Finland) has studied a polyol production process where 100 % of the polyol carbon is originating from $CO_2$. In other words, also the used epoxide is converted from $CO_2$. According to their studies related to the BECCU (Bioenergy Carbon Capture and Utilization) project, a novelty polyol manufacturing process is based on the production of olefins from $CO_2$ and other gases through RWGS and Fischer-Tropsch (FT) reaction steps. Produced olefins are first converted to epoxides using peroxides as an oxidizing agent and then epoxides are polymerized with $CO_2$ to obtain polyols. These polyols are then used in the production of polyurethanes. (VTT b) The description of the process is presented visually in Figure 10.

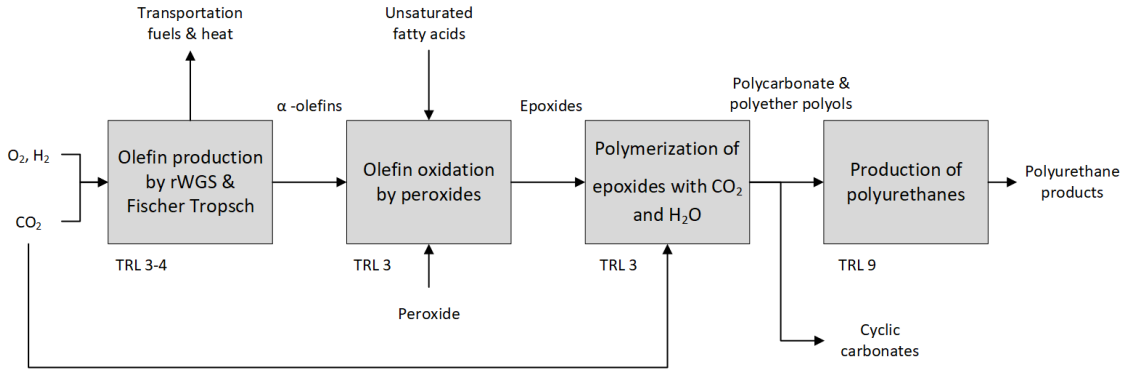



***Figure 10. Process description of polyol production where 100 % of used carbon is originating from captured $CO_2$ (adapted from VTT b).***

As can be seen from the figure, also valuable by-products such as transportation fuels are produced in the VTT's process. These have positive impact on the economic

performance of the process, yet the development of the process steps is varying from TRL-levels of 3 to 9, and thus it is not ready to be commercialized yet.

## 4.4 Others

In this chapter, some significant or interesting applications for the $CO_2$ are presented briefly. Direct utilization routes include $CO_2$ uses in liquid or gaseous form in greenhouses or in enhanced oil recovery (EOR) systems, where $CO_2$ is injected into oil and gas reservoirs to enhance the production of fossil fuels. Actually, the EOR systems are currently the main $CO_2$ utilization industry, but considering the carbon life cycle, these systems still add $CO_2$ into the atmosphere and enhance the use of fossil fuels. The captured $CO_2$ can also be utilized directly in the beverage and food industry as an acidifying agent, but in that case the purity of $CO_2$ is a very significant factor. (Zhang et al. 2020; Rafiee et al. 2018)

In mineralization, industrial $CO_2$ emissions can be effectively utilized to form various products and carbonate precipitates, such as in enhancing the strength and durability of concrete or cement mortars. Depending on the used raw materials and applications, also high-value-added materials, such as geopolymers, abiotic catalysts or soil conditioners, are possible end products. Mineralization can be done with combining $CO_2$ to natural ores, but also alkaline solid wastes are a suitable and especially low-cost feedstock. For example, pulp and paper mill waste or incinerator ashes can be utilized. However, before deployment in a cost-effective manner can be realized, significant technological breakthroughs are required. (Zhang et al. 2020; Rafiee et al. 2018)

In addition to the mineralization of pulp and paper mill waste, pulp mills provide multiple $CO_2$ utilization routes. $CO_2$ can be used in tall oil manufacturing, precipitated calcium carbonate (PCC) production or in lignin separation. However, the utilization possibilities depend on mill-specific details, such as the type of wood raw material and the chosen pulping process. In softwood mills, the tall oil manufacturing would be an option, but in hardwood and eucalyptus mills the levels of extractives are low and therefore the tall oil recovery is rarely done. Lignin extraction can be done in both softwood and hardwood mills, whereas the PCC production is an option in an integrated pulp and paper mill. (Kuparinen et al. 2019)

Biological $CO_2$ utilization or fixation includes various methods to utilize $CO_2$ effectively in mild conditions. Generally, the basic idea is to utilize the natural ability of microorganisms and plants to convert $CO_2$ to biomass as part of the natural carbon cycle. The captured $CO_2$ can be used as a substrate for microorganisms, which can produce compounds that

can be used as chemicals or fuels, such as hydrocarbons, organic acids or bioplastics. Especially microalgae have attracted great attention globally due to their efficient nature: 1 kg of algal biomass can fix about 1.83 kg $CO_2$. (Zhang et al. 2020) In some cases, it is possible to use industrial flue gas directly as a carbon source. For example, in biological wastewater treatment the additional carbon required for microalgae biomass growth can be provided from a point source of $CO_2$ if the temperature of the flue gas is controlled. (Salehizadeh et al. 2020). However, in addition to a highly efficient $CO_2$ fixation ability, in CCU applications microalgae need also ability to survive at high temperatures, at high $CO_2$ concentration and in the presence of other gases such as $NO_x$ and $SO_x$. (Zhang et al. 2020) Therefore, the discovering, selection and genetic modification of the suitable species affect the efficiency of the process.

# 5. TECHNO-ECONOMIC STUDY OF BIOETHANOL PRODUCTION AS A CARBON CAPTURE AND UTILIZATION PROCESS

In this chapter, a techno-economic analysis of bioethanol production as a carbon capture and utilization (CCU) process is described. First, the descriptions of the unit processes are presented, followed by the second part, where the assumptions and calculations for the economic feasibility analysis are described. The analysis has been carried out in MS Excel and it focuses on the mass and energy balances as well as the economic feasibility of the process.

## 5.1 Description of unit processes

In this section, the description of the selected CCU process is performed. The main raw material of the process is flue gas from a lime kiln of a pulp mill and the composition of that gas stream is presented in Table 3. The flue gas is pretreated with a scrubber, where it is cooled down and washed from harmful components, such as particulate matter and $SO_2$, to meet the purification requirements of the carbon capture unit. This pretreatment is left outside the scope of this work to simplify the calculations.

***Table 3. Composition of feed gas from a lime kiln.***

| Parameter | Unit | Value |
|---|---|---|
| Gas flow | kg/s | 25 |
| $N_2$ | wt-% | 52 |
| $CO_2$ | wt-% | 20 |
| $H_2O$ | wt-% | 25 |
| $O_2$ | wt-% | 3 |

The overview of the whole production process from the flue gas to ethanol is presented in Figure 11. First, the flue gas from a pulp mill enters the carbon capture unit, where the $CO_2$ is separated from the gas stream. After that, the $CO_2$ is fed to the RWGS step together with the $H_2$ produced by the water electrolyser. In the RWGS stage, the feed is converted to syngas which is then transported to the fermenter. In the fermentation step, the chosen bacteria convert the syngas to ethanol in aqueous solution. Lastly, the product recovery step containing distillation and molecular sieves is used to get rid of the excess water. The end product of the process is 99.5 wt-% industrial grade ethanol. In addition to ethanol, oxygen is obtained as a by-product from the water electrolysis.

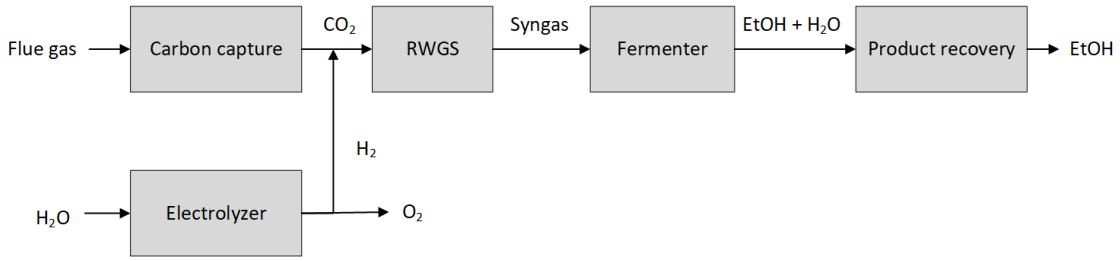



***Figure 11. Process scheme of bioethanol production from captured $CO_2$.***

In the following sections, the unit processes are described in more detailed. The main focus of the calculations is on the RWGS and fermentation steps and their synchronization. Therefore, the other unit processes including the carbon capturing, water electrolysis and the product recovery steps are calculated more generally. All the unit processes are assumed to operate in a steady state and only mass and energy balances are considered. The sizes of the reactors etc. are not taken into account.

### 5.1.1 Carbon dioxide capturing

In the carbon capture unit, the flue gas is treated with an enzymatic-absorption process to separate the $CO_2$ from the gas stream. Absorption has been selected because it is a well-known and effective process compared with other carbon capture technologies. The used solvent is potassium carbonate ($K_2CO_3$), which has advantages such as easy regeneration, low corrosiveness and low tendency to degradation compared with the conventional amine-based solvents. The enzyme is required to increase the reaction rate of the process. The theory behind the process is discussed in Chapter 3.1. The calculations of the unit are based on the reported data by Gilassi et al. (2020), Saunier et al. (2019) and Fradette et al. (2017). Table 4 presents the data collected from the articles including the capture efficiency and the raw material and utility use.

***Table 4. Summary of parameters used in carbon capture unit calculations (Gilassi et al. 2020; Saunier et al. 2019).***

| Parameter | | Value | Unit |
|---|---|---|---|
| Capture efficiency | | 90 | % |
| Chemicals make-up | Enzyme | 0.025 | kg/t $CO_2$ |
| | $K_2CO_3$ | 1.3 | kg/t $CO_2$ |
| | Water | 30 | kg/t $CO_2$ |
| Energy consumption | Electricity | 100 | kWh/t $CO_2$ |
| | Hot water | 3 | GJ/t $CO_2$ |
| By-products | $K_2SO_4$ | 0.4 | kg/t $CO_2$ |
| | $KNO_3$ | 0.00006 | kg/t CO2 |

An overview of the capturing process and equipment is presented in Figure 12. The carbon capture unit consists of two columns, which are the absorber and the stripper. In the absorber $CO_2$ is absorbed in the presence of solvent and a proper catalyst, here potassium carbonate solvent and carbonic anhydrase enzyme. In the stripper the solvent is regenerated for reuse.

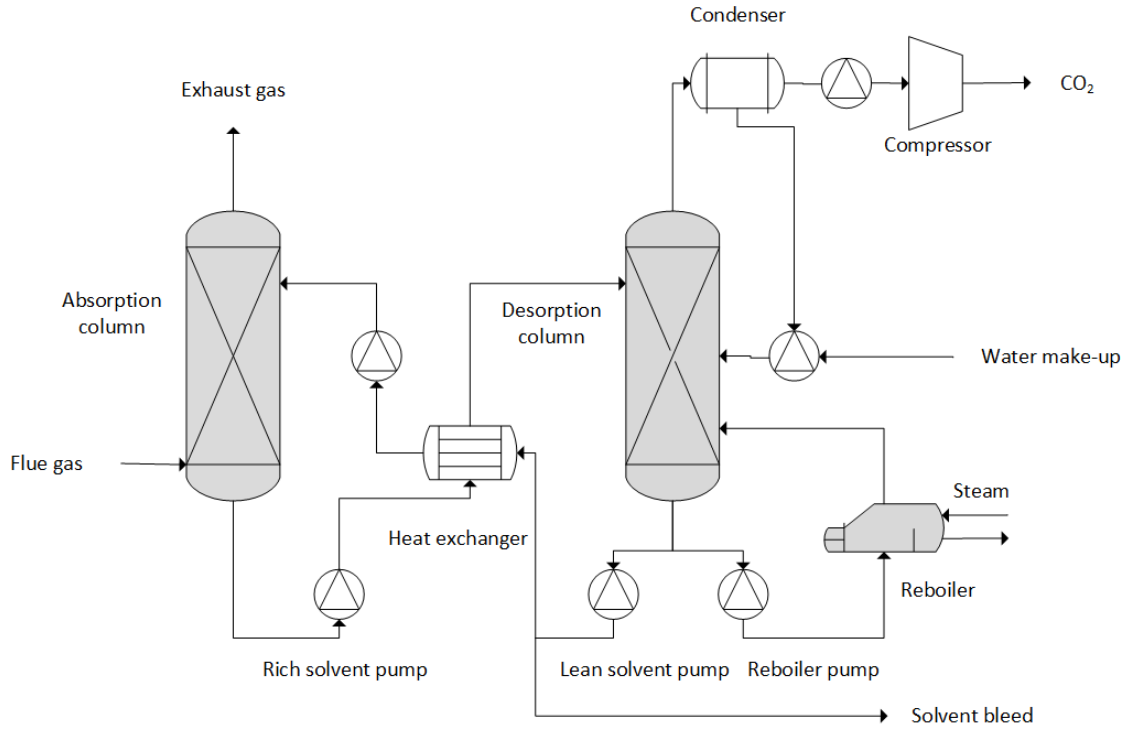



***Figure 12. Process scheme of carbon capture using enzymatic-absorption process (adapted from Saunier et al. 2019).***

The cooled flue gas enters the absorption tower where the lean solvent trickles down the packing. Once the flue gas has travelled up the absorber column, most of the $CO_2$ is absorbed in the solvent and the scrubbed flue gas can be emitted to the atmosphere. The rich solvent solution containing the absorbed $CO_2$ exits at the bottom of the column and is heated by counter-current heat exchanger with the lean solvent, after which it is fed to the stripper column. In the stripper, $CO_2$ is stripped from the rich solvent using hot water from the reboiler. After that, the lean solvent from the bottom of the column is fed back to the absorber column through heat exchangers. The hot and wet $CO_2$ exits at the top of the stripper column and passes through a condenser and a vacuum blower to remove most of the water. Then, the $CO_2$ is compressed and it is ready to be utilized in the further processes. The main by-products of the process are potassium sulfate ($K_2SO_4$) and potassium nitrate ($KNO_3$). (Fradette 2017)

### 5.1.2 Water electrolysis

In this thesis, hydrogen is considered to be generated by a typical alkaline electrolyser according to data from Bellotti et al. (2017). In the process, water molecules are split with electric current to produce hydrogen and oxygen according to the following reaction:

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g). \quad (11)$$

A simplified process description of water electrolysis is presented in Figure 13.

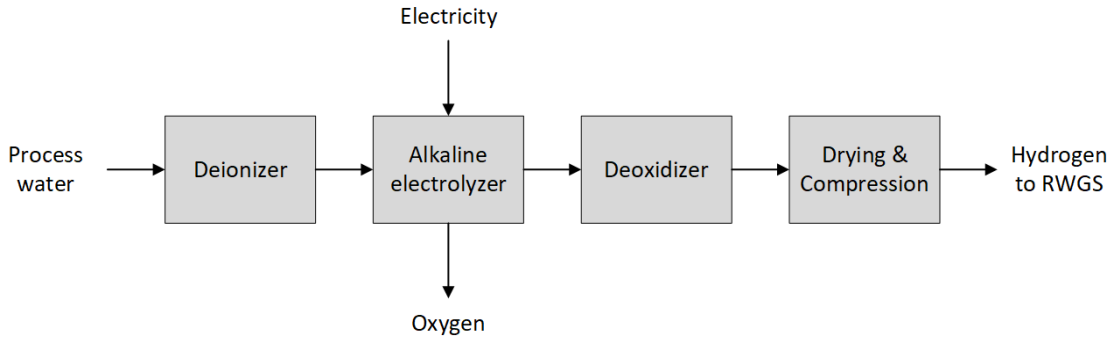



***Figure 13. Process scheme of hydrogen production by water electrolysis (adapted from Godula-Jopek 2015).***

The main raw material of the process is process water, which is treated with deionizer and per each kilogram of $H_2$ generated, 8 kg $O_2$ is formed as a by-product. The purity of both the produced hydrogen and oxygen can be assumed to be 100 % (Hannula 2015). The electricity consumption is 54.2 kWh/kg $H_2$ and it is considered to be from fossil-free sources. Before the RWGS process, hydrogen is dried and compressed.

### 5.1.3 Reverse water gas shift (RWGS)

Reverse water gas shift reaction is used to convert the captured $CO_2$ and $H_2$ into syngas, which is used as a feedstock for the gas fermentation. In the RWGS reaction, $CO_2$ and $H_2$ react to form CO and $H_2O$ according to the following reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O. \quad (12)$$

However, in addition to that reaction, also the Sabatier reaction occurs in the reactor and thus methane ($CH_4$) is produced as a by-product:

$$CO_2 + 4\,H_2 \leftrightharpoons CH_4 + 2\,H_2O. \quad (13)$$

Due to the thermodynamic limitations and endothermic nature of the RWGS reaction, it usually needs to be operated at elevated temperatures (700-900 °C) and pressure up to 3000 kPa to obtain substantial $CO_2$ conversions and avoid forming undesired $CH_4$. (Rezaei & Dzuryk 2019) However, in gas fermentation, the optimal composition of the input syngas contains both CO and $CO_2$. Thus, $CO_2$ conversion in the RWGS does not

have to be as high as possible and temperature can be slightly lower. On the subject of catalysts, it can be expected that the same catalysts, such as commercial zinc oxide/aluminium oxide ($ZnO/Al_2O_3$), which are suitable for water gas shift (WGS) reaction can be used also in the RWGS reaction (Anicic et al. 2014).

The calculations of the RWGS unit process are based on data from Rezaei & Dzuryk (2019) and Bustamante et al. (2004). A simplified flow chart of the process is presented in Figure 14.

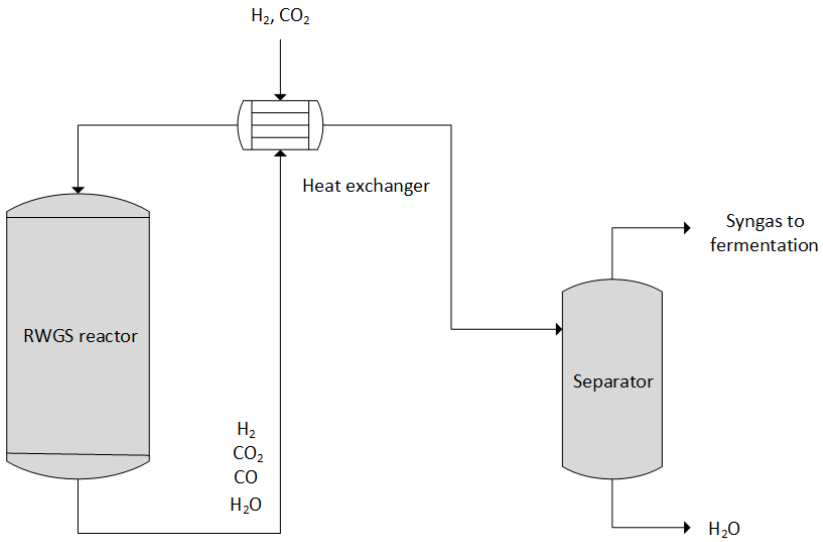



***Figure 14. Process scheme of syngas production in RWGS reactor (adapted from Samimi et al. 2019).***

First, the feedstock gas mixture containing $CO_2$ and $H_2$ is fed to the adiabatic RWGS reactor, where $CO_2$ and $H_2$ are partially converted to CO and $H_2O$ in the presence of a catalyst. Then the product stream containing syngas and $H_2O$ is conveyed to the fermenter via the separator. There is no need to remove water from the stream because the fermentation reactions occur in aqueous solution. However, the output stream goes through a heat exchanger, where the excess heat of the process is used to heat up the input gases. When the output gas mixture gets cooler, part of the water will condensate, but the condensed water is utilized in the fermentation process.

### 5.1.4 Ethanol fermentation and product recovery

In the fermentation step, the syngas produced in the RWGS process is converted to ethanol via reactions mediated by enzymes inside the living cells. The theory behind the gas fermentation is discussed in Chapter 4.1. Here, the calculations of the fermentation and product recovery steps are based on data from Pardo-Planas et al. (2017), Piccolo & Bezzo (2009), Medeiros et al. (2017) and Vane (2008).

The fermenter is operated at atmospheric pressure and 37 °C. The temperature is the optimal temperature for growth of ethanol-producing acetogenic microorganisms, here *Clostridium ragsdalei*. Additionally, low operating temperatures are beneficial because the energy required for heating is lower and the solubility of the substrate gases increases at lower temperature. (Pardo-Planas et al. 2017) The fermenter consists of the reactor and cells of the acetogenic bacteria in cell broth. A flow chart of the process is presented in Figure 15.

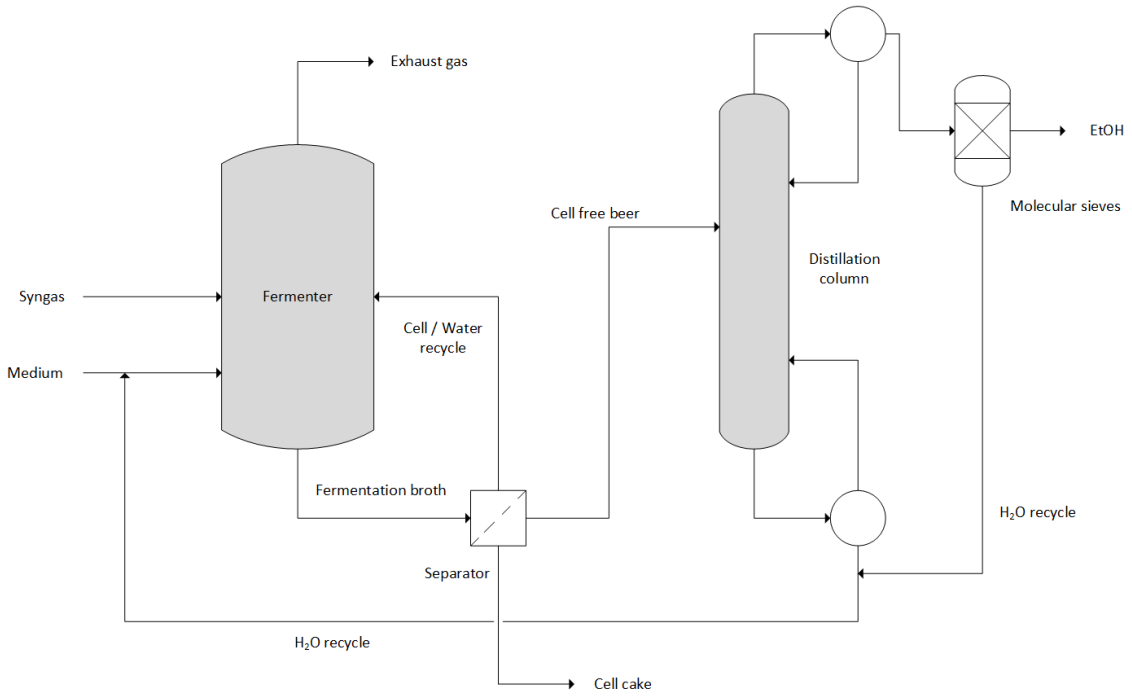



***Figure 15. Process scheme of syngas fermentation to ethanol (adapted from Pardo-Planas et al. 2017).***

The input streams to the fermenter are syngas from the RWGS process and liquid medium containing mostly water and important nutrients for the cell growth. Here, the main nutrient is ammonium chloride ($NH_4Cl$) and the others are considered to be negligible. The pH buffering is done by acetate-acetic acid system, since acetic acid is produced as a by-product. Microorganisms are known to be capable to convert acetic acid to ethanol and therefore, acetic acid concentration is considered to remain stable. This addition to the ethanol production is, however, negligible.

The product stream from the fermenter is a mixture of liquid and gas, which needs to be separated with minimizing the ethanol lost in the exhaust gas. A high cell concentration is reached with a cell recycle system, which returns the filtered cells from the broth back to the fermenter. However, a purge stream is necessary to avoid accumulation of cell mass in the system. To reduce the ethanol loss in the purge stream, the cells are

concentrated and separated out as a cell cake while rest of the broth is recovered back to the process.

Finally, the liquid broth is sent to the product recovery unit, where it is treated using a combination of conventional distillation and molecular sieve adsorption to obtain anhydrous ethanol (99.5 wt-%). In the first step, the broth is distilled to the ethanol purity of 92.4 wt-% and then the remaining water is removed using packed beds of molecular sieves. The water and acetic acid from the recovery step are recycled back to the fermenter to minimize the water consumption, and nutrient and product loss in the process.

## 5.2 Assumptions and calculations for economic analysis

In this section, the assumptions and calculations for the economic analysis are described. First, the theory and equations behind the capital expenditures and operational expenses calculations are presented. After that, the measures for the evaluation of the economic feasibility of the process are described and lastly the procedure for the scenario analysis is presented. General information of the values used in the calculations is collected in Table 5. The values are universal information in the energy and process sector.

***Table 5. General assumptions for economic analysis.***

| Parameter | Value | Unit |
|---|---|---|
| Operational years | 30 | a |
| Operating hours | 8000 | h/a |
| Inflation rate | 1.34 | % |
| Discount rate | 10 | % |
| Interest rate | 10 | % |
| Reference year | 2020 | |

The production capacity of the plant is assumed to be constant during the operational years. Additionally, the inflation is taken into account when the CAPEX is scaled from past to the reference year. However, inflation or escalation of utilities or raw materials in the future is not considered.

### 5.2.1 Capital expenditures

Capital expenditures (CAPEX) are costs that are caused by the major purchases, such as buildings and equipment, that are designed to be used over the long-term. Here, the CAPEX includes the purchasing of installed equipment.

The CAPEX is estimated using data from literature and the media. If the capacity level of the equipment found in literature differ from the ones used in this thesis, the cost is estimated using the following equation (Tribe & Alpine 1986):

$$C = C_{ref} * \left(\frac{V}{V_{ref}}\right)^{\alpha}, \quad (14)$$

where *C* denotes the equipment cost, *V* the capacity of the equipment and *α* the scale coefficient. The value of α = 0.6 is often used as a rule of thumb if exact data is not available.

If the costs were originally given in foreign currency, they are exchanged into euro using the values given in Table 6.

***Table 6. Values of exchange rates.***

| Currency | Value |
|---|---|
| Euro (€) | 1 |
| United States Dollar (USD) | 1.19 |
| Canadian dollar (CAD) | 1.56 |

Furthermore, if the costs found in literature are from different year, they are scaled to the reference year of this thesis using equation (Vernimmen et al. 2014, p. 270):

$$C = C_0 * (1 + i)^n, \quad (15)$$

where $C_0$ denotes the initial equipment cost, *i* means the inflation rate and *n* is the number of years.

### 5.2.2 Operational expenses

Operational expenses (OPEX) are costs that are caused by the operation of a plant and assumed to occur annually during the operational years. Here, the OPEX consists of maintenance and indirect costs, raw materials and utilities. The summary of the main operational expenses of the studied process is presented in Table 7.

***Table 7. Summary of costs of main utilities and raw materials of the process.***

| Parameter | Value | Unit | Reference |
|---|---|---|---|
| Maintenance + indirect costs | 5 % of CAPEX | | Raiko 2020 |
| Electricity | 40 | €/MWh | Nordpool Group |
| Hot water | 3.8 | €/MWh | Mansikkasalo 2020 |
| Steam | 7.6 | €/MWh | Mansikkasalo 2020 |
| Process water | 1.3 | €/m3 | Turun Vesihuolto, Kymen Vesi, HSY |
| Deionized water | 4 | €/m3 | Hilden 2020 |
| Flue gas | 0 | €/t | |
| $CO_2$ | 40 | €/t | Hannula 2015 |
| Enzyme | 400 | €/kg | Gilassi 2020 |
| Potassium carbonate | 420 | €/t | Gilassi 2020 |
| Ammonium chloride | 35.4 | €/kg | Merck |

The cost of $CO_2$ realizes only in the case, where the carbon capture unit is replaced with purchased $CO_2$. Transportation, waste disposal, wastewater treatment and storage costs are ignored, because the effects of those on the results is negligible. Additionally, the costs of the catalysts for RWGS and fermentation (bacteria) are not considered, because the prices are not universally available.

### 5.2.3 Economic feasibility

The economic feasibility of the studied process is estimated using some basic measures, which are presented in this chapter. Levelized cost of fuel or energy indicates the average net present cost of fuel production or energy generation for a plant over its lifetime. It is calculated as the ratio between the annual costs divided by the annual output from the plant. First, the capital charge is annualized with the following equation (Smith 2005):

$$C = C_{total} * \frac{i(1+k)^n}{(1+k)^n - 1}, \tag{16}$$

where $C_{total}$ denotes the total capital cost of the project, $n$ is the number of operational years and $k$ is the interest rate. After that, the levelized cost of ethanol production can be evaluated according to the following equation (Hannula 2015):

$$LCOEtOH\left(\frac{€}{L}\right) = \frac{F + E + C + O - R}{P}, \tag{17}$$

where $F$ is the annual cost of feedstock, $E$ is the annual cost of energy, $C$ is the annualized capital charge, $O$ is the annual operating and maintenance costs and $R$ is the annual revenue from selling by-products. $P$ denotes the annual output of ethanol from the plant. If LCOEtOH is compared with the current market price of ethanol, the

competitiveness of the studied process compared with existing processes can be estimated.

The payback period is a method to calculate a rough assessment of the profitability and risk of an investment. It indicates how many years it takes for the net cash flow to recover the initial outlay on an investment. The payback period can be calculated according to the following equation (Vernimmen et al. 2014):

$$Payback\ period = \frac{Total\ investment}{Net\ annual\ cash\ flow}\ . \tag{18}$$

The analysis of the results is simple: The shorter the payback period is, the better. Especially, in the case of very high-risk investments it is desirable to get the invested money back before it is too late. Payback period is, however, a very rough method and it ignores the time-value of money and the cash flows after the payback period. Thus, it may lead to wrong conclusions. (Vernimmen et al. 2014)

The net present value (NPV) is a simple method for estimating the profitability of an investment, but compared with the payback period method, it takes the time value of money into account. The NPV is the difference between the discounted annual cash flows and the investment, and can be calculated according to the following equation (Vernimmen et al. 2014):

$$NPV = \sum_{t=1}^{n} \frac{X_t}{(1+r)^t} - I. \tag{19}$$

In the equation, $X_t$ is the net cash flow at the end of the year *t*, *r* is the applied discounting rate, *n* is the investment time and *I* is the investment value. If the NPV is positive, the investment is profitable with the discounting rate used. With this method, the annual cash flows are discounted to the present year and in addition to the NPV, these can be utilized to calculate the discounted payback period. Compared with the ordinary payback period, it remedies the time value of money. (Vernimmen et al. 2014)

The yield of an investment can be estimated with the internal rate of return (IRR). It tells the discounting rate at which the market value of an investment is equal to the present value of the investment's future cash flows. The IRR can be calculated using the NPV formula (Equation 19) and making the discounting rate *r* unknown. By solving the *r*, the case when the NPV is zero will be found. If the IRR is higher than the applied discounting rate on the investment, the project is profitable. (Vernimmen et al. 2014)

### 5.2.4 Scenario analysis

In the scenario analysis, the effects of chosen parameters on the process costs are investigated to find out what the uncertainty of the results is. The examined parameters are the production plant size, the cost of $CO_2$, the selling price of $O_2$ and electricity price. The used values of those parameters are presented in Table 8.

***Table 8. Values of variable parameters for scenario analysis.***

| Parameter | Option A | Option B | Option C |
|---|---|---|---|
| Plant size | 22 ML/a | 45 ML/a | 90 ML/a |
| Cost of $CO_2$ | 0 €/t | 40 €/t | |
| $O_2$ selling | $O_2$ is not sold | $O_2$ is sold at 100 €/t | |
| Cost of electricity | 30 €/MWh | 40 €/MWh | 50 €/MWh |

In the economic calculations, the OPEX increases and decreases linearly meaning that the changes in the plant size do not affect the formation of costs per litre ethanol. However, the CAPEX is dependent on the capacity of the process and therefore the plant size changes have an effect on the levelized cost. Thus, compared with the base case plant (45 million litres of ethanol in a year), the plant sizes are varied from a half-sized plant (22 ML/a) to a double-sized (90 ML/a).

The second examined parameter is the cost of $CO_2$. In the base case, the $CO_2$ is captured with the carbon capture unit and thus, the raw material cost of $CO_2$ is 0 €/t, but the capture unit incurs both capital and operational expenses. In the option B, the carbon capture unit is replaced with ready-made $CO_2$, which is purchased at the price of 40 €/t. This indicates, whether it is more profitable to own a carbon capture unit or to pay for someone else to do that, because $CO_2$ purchasing decreases the CAPEX significantly but at the same time increases the OPEX.

The third parameter is the selling of the by-product $O_2$ from the water electrolysis unit. In the base case the $O_2$ is not sold so the process does not have additional revenues. In the option B, the $O_2$ is sold at the price of 100 €/t, which decreases the levelized cost. The last parameter is the cost of electricity, which varies from 30 €/MWh to 50 €/MWh indicating the changes in the electricity market.

# 6. RESULTS

In this chapter, the results of the techno-economic analysis are presented. The technical performance and economical results are presented first and after that, the effects of different parameters on the outcome of the overall process are evaluated in the scenario analysis.

## 6.1 Technical performance

The calculations of the technical performance are based on the amount of $CO_2$ entering the carbon capture unit. When the $CO_2$ feed to the process is 5.4 kg/s, 1.5 L of 99.5 wt-% ethanol is produced per second. It equals the annual $CO_2$ consumption of 150,000 t and ethanol production of 43.6 ML. Thus, 280 L of ethanol per ton of $CO_2$ is obtained. Table 9 shows the overall material balance and energy duties of the process.

***Table 9. Overall material balance and energy duties of the process.***

| **Inputs** | **Process** | **Material** | **t/a** |
|---|---|---|---|
| | Carbon capture | $CO_2$ | 156 480 |
| | Carbon capture | Enzyme | 4 |
| | Carbon capture | Potassium carbonate | 177 |
| | Carbon capture | Process water | 3 949 |
| | Electrolyser, Fermentation | Deionized water | 215 707 |
| | Fermentation | Ammonium chloride | 58 |
| **Outputs** | **Process** | **Material** | **t/a** |
| | Carbon capture | $K_2SO_4$ | 50 |
| | Carbon capture | $KNO_3$ | 0.008 |
| | Electrolyser | $O_2$ | 83 537 |
| | RWGS | $CH_4$ | 105 |
| | Fermentation | $CO_2$ | 63 112 |
| | Fermentation | CO | 1 046 |
| | Fermentation | $H_2$ | 731 |
| | Electrolyser, Fermentation | Wastewater | 121 645 |
| | Fermentation | Acetic acid | 1 705 |
| | Fermentation | Biomass | 4 063 |
| | Distillation | Ethanol | 34 393 |
| **Energy duties** | **Process** | **Energy** | **MW** |
| | Carbon capture, Electrolyser, RWGS, Fermentation | Electricity | 76 |
| | Carbon capture | Hot water | 14 |
| | Distillation | Steam | 10 |

As can be seen, the major raw materials for the process are deionized water and flue gas containing $CO_2$. Production of deionized water is not included in the calculations. It is considered raw material, which can be bought ready-made. From the outputs, the most significant ones in addition to ethanol are wastewater, $O_2$ and $CO_2$. The processing of those streams is discussed in the following paragraphs.

In the carbon capture unit, the $CO_2$ capture efficiency is 90 %. In addition to the $CO_2$ stream, the carbon capture unit yields small amounts of $K_2SO_4$ and $KNO_3$, which are ionic compounds of potassium in a liquid form. Those are considered harmless compounds that can be conveyed directly to a conventional wastewater treatment plant. The carbon capture unit consumes 2 MW of electricity and 14 MW of hot water.

In the water electricity unit, the deionized water is converted to $H_2$ with the conversion efficiency of 0.60. Additionally, 84,000 t of $O_2$ is produced as a by-product annually. The unreacted deionized water is expected contain solute impurities from the process and therefore it is transferred to a wastewater treatment plant. The reuse of the unreacted water could be possible, but it requires additional purification steps and thus it is not calculated here. The electricity consumption of the water electrolysis unit is 71 MW.

In the RWGS step, the inputs are $CO_2$ and $H_2$ with the ratio 0.38 and 0.62, respectively, while the output is syngas stream containing CO, $H_2$, $CO_2$, $H_2O$ and a little $CH_4$. Since the amount of produced methane is small ($0.78 * 10^{-3}$ mol/mol syngas), it is excluded from the more detailed study.

For the fermentation, the optimal composition of the syngas to maximize the ethanol production is approximately 30 mol-% CO, 35 mol-% $H_2$ and 30 mol-% $CO_2$, in which case $H_2$/CO ratio is 1.2 (Pardo-Planas et al. 2017) However, as a biological process, the effect of the exact composition of the input syngas on the fermentation is not as considerable as for the Fischer-Tropsch synthesis, for instance. Bacteria can tolerate a little variation to keep the process running. Here, the composition is optimized between the $CO_2$ conversion efficiency and energy consumption of the RWGS stage. The optimal $CO_2$ conversion is solved to be 0.50. It could be higher, but then the energy consumption increases, in which case the effect on the efficiency of the process is cancelled out. Thus, the result is syngas containing 20 mol-% CO, 40 mol-% $H_2$ and 20 mol-% $CO_2$ and $H_2$/CO ratio of 2.3.

The temperature of the feed to the RWGS stage is 25 °C. It is heated up to the reaction temperature 700 °C by transporting the output stream through a heat exchanger. The efficiency of the heat exchanger is 90 %, and the rest required heating is performed by electricity. The electricity consumption of the RWGS stage is 3 MW.

In the fermentation, the main inputs in addition to the syngas stream are the growth medium containing ammonium chloride as a nitrogen source for the bacteria and the recycle stream. As mentioned, the composition of the input syngas can vary a little. However, the conversion of carbon to ethanol depends on the used bacteria, but also on the carbon source. CO can perfom as the sole carbon and energy source, but $CO_2$ conversion depends on additional energy source, here $H_2$. Therefore, CO conversion is energetically preferred. The conversions to ethanol are 0.81 to CO and 0.88 to $H_2$, respectively. It is assumed that in the base case, 10 % of CO is consumed to biomass growth. Thus, the cell concentration of 3.5 g/L is obtained. Table 10 shows a summary of the main process parameters. Additionally, pressure and temperature affect the mass transfer rate of gaseous substrates into the medium, which have an effect on the specific gas uptake by the bacteria and thus to the ethanol production. The more detailed examination of these parameters is, however, excluded from the calculations. The process conditions in the fermenter are expected to be close to the ambient conditions.

***Table 10. The main process parameters of the fermentation.***

| Parameter | Value | Unit |
|---|---|---|
| Cell concentration | 3.5 | g/L |
| $NH_4Cl$ concentration | 1 | g/L |
| EtOH concentration | 30 | g/L |
| CO conversion to EtOH | 0.81 | |
| $H_2$ conversion to EtOH | 0.88 | |

Since the fermentation occurs in liquid medium, the amount of the used water is significant. The water consumption is minimized with the cell recycle loop and by reusing the separated water from the distillation. The amount of fresh water needed for the fermentation is 1.7 kg/kg EtOH. In addition to the liquid broth, the main outputs from the fermenter are a cell cake and gases. The cell cake is removed biomass, which is pressed to remove most of the water from the mass. The amount of the cell cake produced in the fermentation is 0.12 kg/kg EtOH. It can be utilized as a fertilizer, for instance, but the end-uses of the cell cake are not considered here. The output gas stream contains unreacted syngas and a significant amount of $CO_2$ produced during the fermentation. However, the processing of the output gas stream is not either considered here. The unreacted syngas could be used in energy production while the $CO_2$ could be reused in the RWGS stage. However, it requires additional processing steps, such as separation and compression and therefore it is excluded.

Fermentation is an exothermic reaction, which means that it releases energy. To keep the fermenter temperature constant and bacteria alive, a cooling system is required. The cooling is carried out with lake water and the electricity consumption of the pumping system is 0.05 kW. In the product recovery step, the energy consumption depends mostly on the ethanol concentration in the broth. Here, the reached ethanol concentration is 30 g/L, which is quite low in comparison with the conventional fermentation. However, for the gas fermentation process it is normal. The steam consumption of the product recovery is 10 MW.

## 6.2 Economic results

In the following sections, the economic results of the base case process are presented. First, the CAPEX and OPEX are presented, and after that those results are utilized in the evaluation of the economic feasibility. In the scenario analysis section, some process parameters are varied to evaluate the profitability of the process more.

### 6.2.1 Capital expenditures

The CAPEX is calculated according to Equations 14 and 15. For the water electrolysis and RWGS stages, the used scale coefficients are 0.93 and 0.67 according to Hannula (2015), whereas in the case of the carbon capture and fermentation units the general value of $\alpha = 0.6$ is used. Additionally, in the fermentation product recovery stage only distillation vessels are included, since the effect of the molecular sieves on the total sum is considered negligible. The results for each unit process are presented in Table 11. However, the presented numbers are rough approximations, whose uncertainty is high, because the technologies are still in the development stage and therefore the precise information on investment costs is hard to find. The CAPEX of the whole process is 83.6 M€, which corresponds roughly to an investment in a new 80 MW gas fired power plant or 10 % of an investment in a new average pulp mill (Matthis 2019; Taponen 2019).

***Table 11. Summary of capital expenditures (CAPEX) of the unit processes.***

| Unit process | Value | Unit | Reference |
|---|---|---|---|
| Carbon capture | 24.4 | M€ | Cleantech Canada Staff 2016 |
| Water electrolysis | 48.1 | M€ | Hannula 2015 |
| RWGS | 4.3 | M€ | Hannula 2015; Kreutz et al. 2005 |
| Fermentation + Distillation | 6.8 | M€ | Piccolo & Bezzo 2009 |
| Total | 83.6 | M€ | |

The distribution of the total CAPEX is presented in Figure 16. The major part (58 %) of the CAPEX consists of the electrolyser. The second largest unit process is the carbon capture unit with the share of 29 % while the RWGS and fermentation stages have minor effect on the total sum.

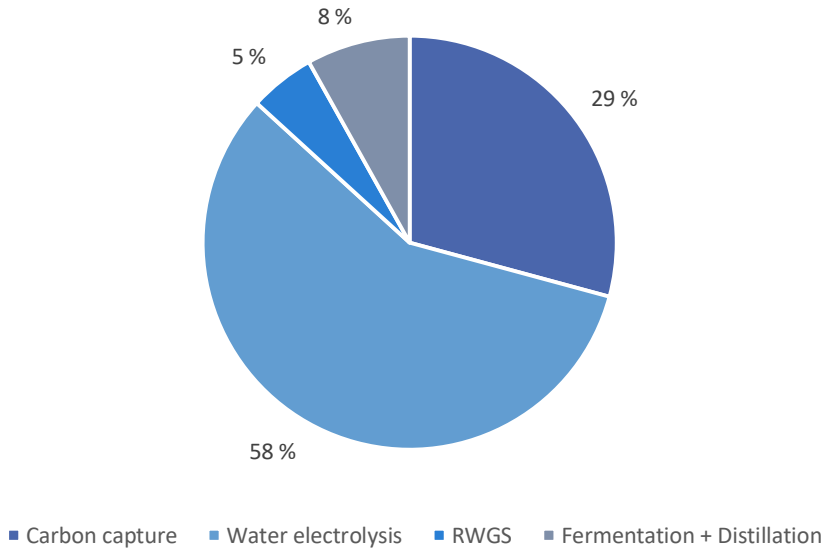



***Figure 16. Distribution of the CAPEX between the unit processes.***

This result is probably the consequence of the different TRL-levels and the complexity of the unit processes. The carbon capture and water electrolysis are technologies still under development, whereas the RWGS and fermentation are more or less commercial technologies. For example, compared with distillation, which is energy-intensive, but still commonly used and mature technology, the prices of the water electrolysis vessels are still high, because the number of suppliers is low. However, in the future, the situation will change since the universal interest in the $H_2$ production and utilization is significant.

Secondly, compared with the carbon capture, the fermentation occurs at low temperature and atmospheric pressure and therefore the used construction materials can be more economical. Additionally, depending on the chosen reactor type, the fermenter vessel can be quite simple, and it is just a single vessel. Bubble column reactors, for instance, do not contain any additional mixer since the bubbles take care of the mixing, while the absorption-based carbon capture requires two columns and a reboiler.

### 6.2.2 Operational expenses

The OPEX of the process is based on the price information given in Table 7 and material and energy balance given in Table 9. The results are collected to the following Table 12.

***Table 12. Summary of the main operational expenses (OPEX) of the process.***

| **Fixed** | | | **€/a** |
|---|---|---|---|
| | | Maintenance, Indirect cost | 4 180 913 |
| **Variable** | **Energy** | | **€/a** |
| | | Electricity | 24 331 584 |
| | | Steam | 626 435 |
| | | Hot water | 395 023 |
| **Variable** | **Raw materials** | | **€/a** |
| | | $CO_2$ | 0 |
| | | Enzyme | 1 413 908 |
| | | Potassium carbonate | 74 528 |
| | | Process water | 5 147 |
| | | Deionized water | 862 829 |
| | | Ammonium chloride | 2 052 028 |
| Total | | | 33 942 396 |

The following Figure 17 shows the distribution of the annual variable costs between the unit processes. As can be seen, the most significant factor is the energy consumption of the water electrolysis unit. The cost of 22.8 M€ is 75 % of the annual variable costs of the overall process while the sum of the other raw material and energy costs is only 7 M€.

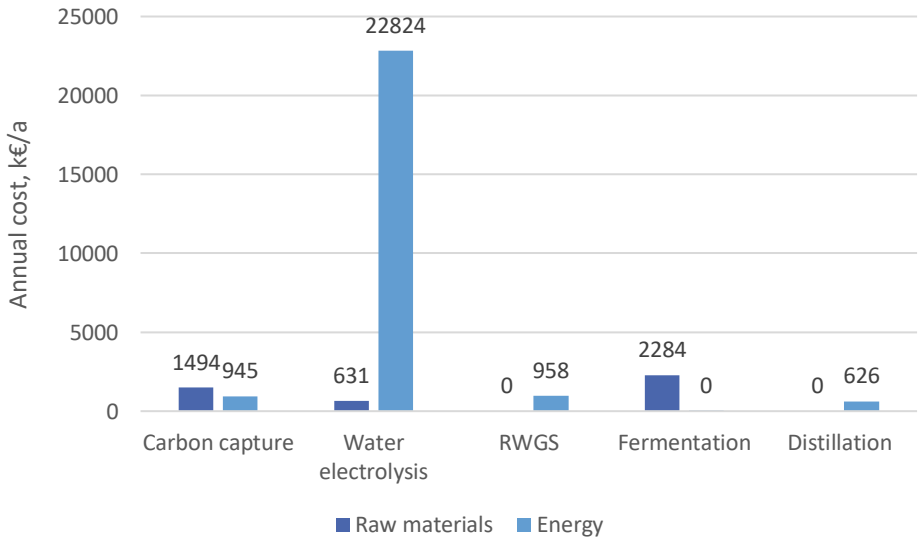



***Figure 17. Distribution of annual variable costs between the unit processes.***

From the raw materials, the most significant costs are enzyme and ammonium chloride, which are used as a catalyst in the carbon capture and as a nutrient in the fermentation. Even though the annual cost of those together is 3.5 M€, it is only 17 % of the cost of electricity of the water electrolysis. The same observation can be done with the other raw

materials or energy sources: compared with the total cost of the electricity, the effects on the total sum are only minor.

### 6.2.3 Economic feasibility

The levelized cost of the produced ethanol is calculated using Equations 16 and 17. However, taxation is excluded from the calculations. In the base case, the LCOEtOH is 0.98 €/L. The distribution of the levelized cost is presented in Figure 18. As can be supposed, the major part of the costs come from energy with the share of 59 %. The second largest part is capital charge with the share of 21 % while the feedstock as well as the maintenance and indirect costs are smaller parts. In the base case, the by-products are not sold and therefore the revenue is null.

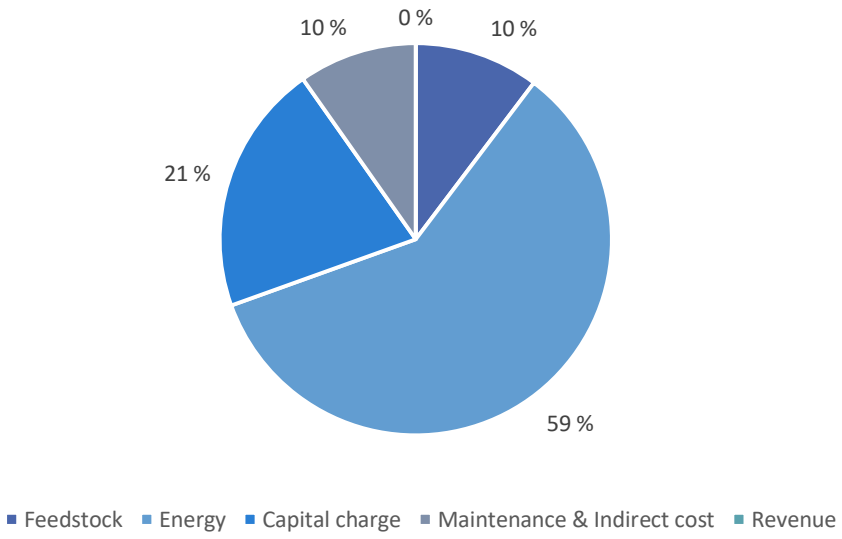



***Figure 18. Distribution of levelized cost of the produced ethanol.***

Compared with the current market price of the industrial grade ethanol, which is 0.65 €/L, the levelized cost in the base case is too high to the process to be profitable (Pennington 2018; Budimir et al. 2011). Additionally, if taxation would be included, the levelized cost would be even higher and the process further from profitability. The other feasibility indicators presented in Chapter 5.2.3 indicate the same result. Figure 19 shows the annual revenues and expenses visually, when the selling price of ethanol is 0.65 €/L.

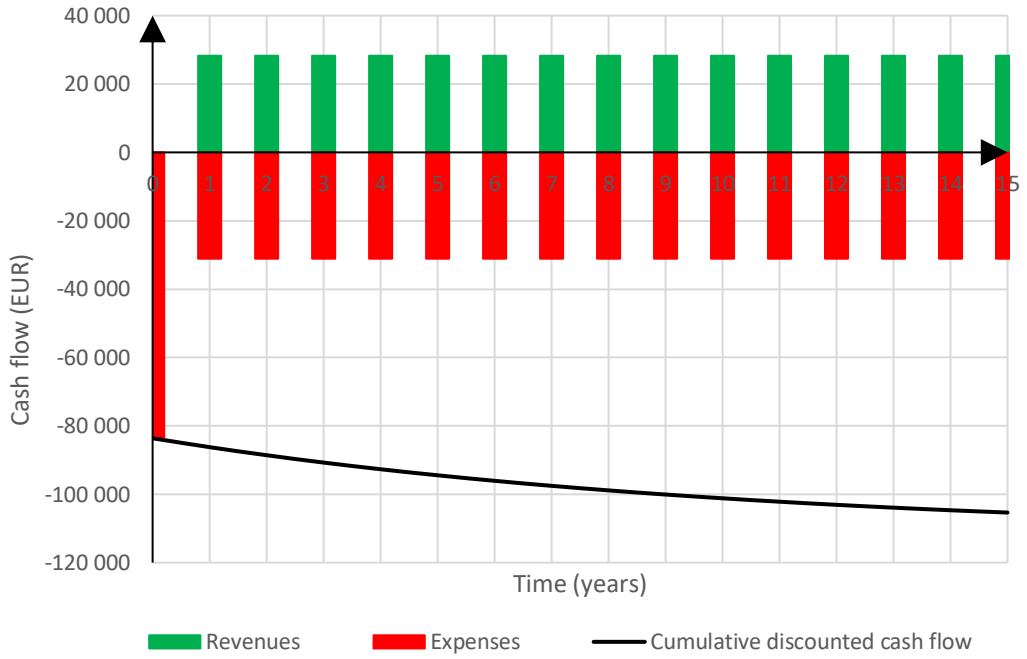



***Figure 19. Annual revenues and expenses of the base case process.***

Because the expenses are higher than the revenues, the cumulative discounted cash flow is negative and therefore the total investment costs cannot be amortized. Since the cash flow is negative, it is not possible to calculate the payback period for the base case process. However, from Figure 19 can be seen that the unprofitably of the process is a result from both too high CAPEX and too high OPEX. To make the payback period realistic or at least less than 10 years, the annual revenues should be significantly higher than the annual expenses to compensate the capital investment of 83.6 M€. But even though the CAPEX would be lower, the annual raw material and energy price per litre alone is higher than the market price of ethanol meaning that the process does not turn a profit. The NPV indicates the same result: after five years, the NPV is -94,500 € and after ten year as much as -101,000 €. Since in this case, the investment does not yield, it is not sensible to calculate the IRR value.

### 6.2.4 Scenario analysis

In this section, the effects of the chosen parameters on the process costs are investigated. The examined parameters are the production plant size, the cost of $CO_2$, the selling price of $O_2$ and electricity price. The influence of $CO_2$ purchasing and $O_2$ selling on the levelized cost of ethanol is presented in Figure 20.

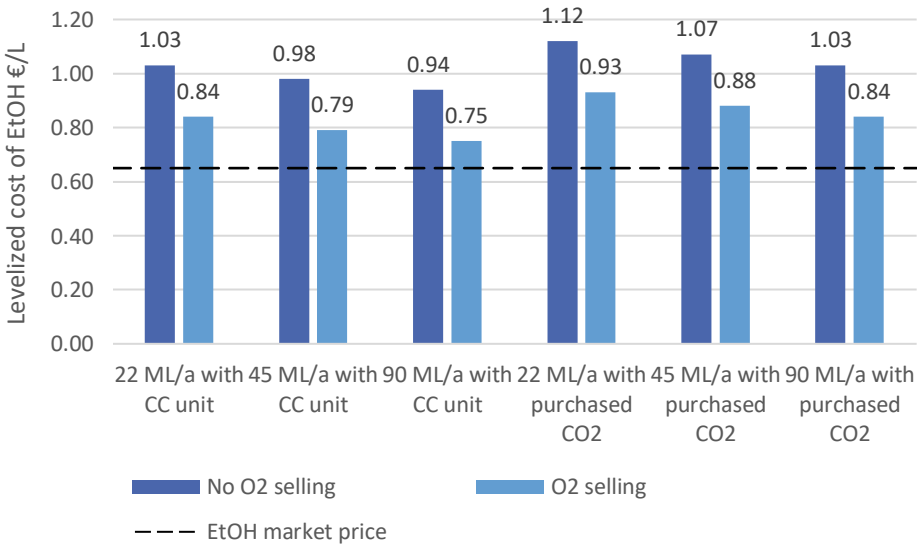



***Figure 20. Influence of $CO_2$ purchasing and $O_2$ selling on levelized cost of ethanol.***

As can be seen, the purchasing of $CO_2$ increases the levelized cost systematically. Thus, it can be concluded that in every case, it is more profitable to include the carbon capture unit to the production plant instead of paying for somebody else to do that. Naturally, if the price of $CO_2$ is cheaper, the situation may change. As for the $O_2$ selling, the levelized cost decreases 0.19 €/L in every case. Depending on the starting point, it is about 20 % of the levelized cost and thus quite good improvement. In the best case, which is 90 ML/a plant with a carbon capture unit and $O_2$ selling, the levelized cost is 0.75 €/L. However, despite the improvement, it is still higher than the market price of ethanol.

Figure 21 presents the influence of the electricity price on the levelized cost. The change of 10 €/MWh in the electricity price decreases or increases the levelized cost with 0.15 €/L. Again, the big plant gives the best results. When the electricity price is 30 €/MWh, the levelized cost of ethanol is 0.80 €/L, which is a good trend to the cost-effective process, but not enough. At the same time, if the electricity price remains stable or in the worst scenario increases, there is no way for the process to be profitable.

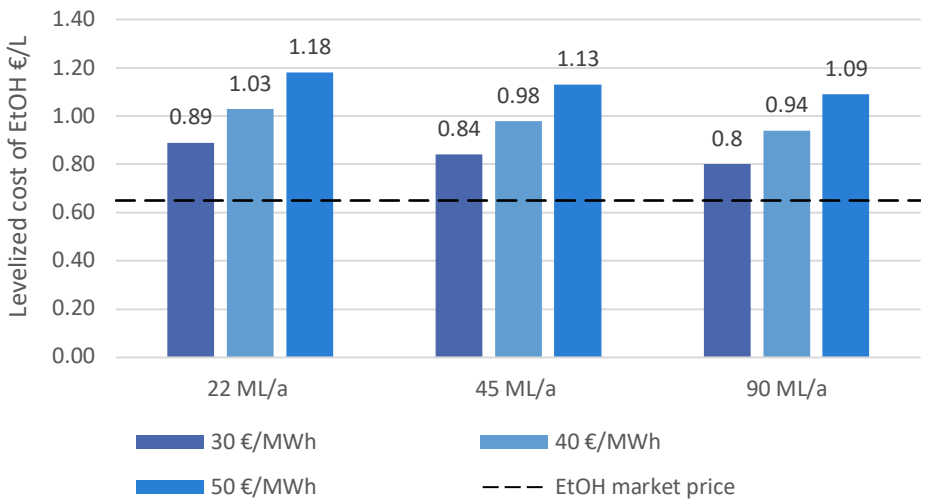



***Figure 21. Influence of electricity price on levelized cost of ethanol.***

Since none of the single parameters alone resulted in a competitive levelized cost for the produced ethanol, a case with multiple optimized parameters is investigated as well. If the plant size is 90 ML/a, the electricity price is 30 €/MWh and the by-product $O_2$ is sold, levelized cost of 0.61 €/L is obtained (the case A). However, as mentioned before, the unprofitability of the process is a result of both too high CAPEX and too high OPEX. Therefore, if the other parameters are unchanged and the CAPEX is expected to decrease to 75 % from the original value, the levelized cost is 0.54 €/L (the case B). As can be seen from Figure 22, both of these values are competitive to the market price of industrial grade ethanol. However, if the reference is fuel grade ethanol with a market price 0.45 €/L, there is still a gap between the prices. The fuel grade ethanol is included in the figure as a reference, because the ethanol grade depends only on the production recovery step and thus the production process is almost the same.

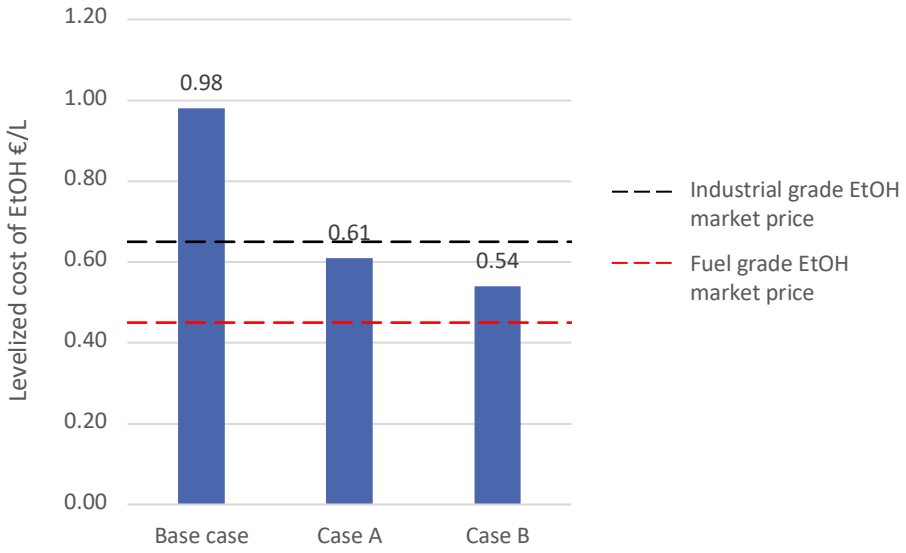



***Figure 22. Comparison of levelized cost of different cases with market prices of ethanol.***

Since the levelized cost of the cases A and B are competitive to the ethanol market price, it is sensible to evaluate the profitability with the other economic feasibility indicators. For the case A, the discounted payback period is 10 years, which is a quite long time period for a new technology investment. Additionally, after 10 years the NPV value is lightly negative, -380 €, indicating an unprofitable process. When the used discount rate is 10 %, the IRR value of 9.9 % indicates the same conclusion. If the time period under observation was 15 years, the case A would be a definitely profitable process. However, as mentioned before, the payback period should be as short as possible and therefore a process of this kind would not be implemented.

For the case B, the discounted payback period is 6.5 years. After 7 years, the NPV is 5,866 € and the IRR is 12 % indicating a profitable investment. Figure 23 shows the annual revenues and expenses of the case B visually, when the selling price of ethanol is 0.65 €/L. In comparison with Figure 19 and the base case process, the case B seems significantly more promising.

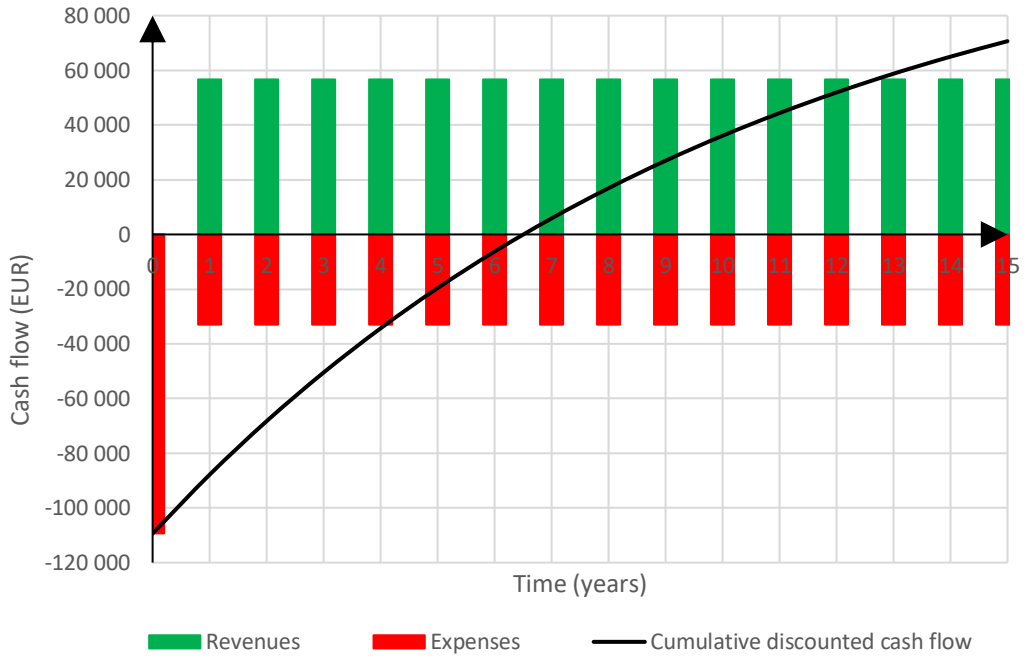



***Figure 23. Annual revenues and expenses of the case B project.***

However, the profitability of the process is highly dependent on the market price of ethanol, because depending on the $O_2$ selling, it is the only revenue. If the trend continues similar, the market price of ethanol will still decrease in the future meaning that the requirements for the profitable process will become even more stringent, especially if the time period under observation is long. According to Matthis (2019), UPM's 95 million investment in a new gas fired power plant in Germany has a payback time of 3 years. In comparison to that project, it is hardly to believe that the case B with the 110 M€ capital investment and the payback period of 6.5 years would be implemented.

# 7. DISCUSSION

In the previous sections, a process converting captured $CO_2$ from flue gas to 99.5 wt-% ethanol is introduced and both the technical performance and economic results of the process are presented. In the base case, the levelized cost of 0.98 €/L ethanol is obtained while the current market price for the industrial grade ethanol is 0.65 €/L. In comparison of those two values it is clear that in the base case the studied process is not competitive. The other economic feasibility indicators give the same result. However, the upside is that the most significant factor is easy to find: a huge electricity consumption of the water electrolysis unit. The same unit also causes 60 % of the capital expenditures.

As can be noticed from the scenario analysis, the changing of a few parameters results in a more profitable process. If the parameters are changed one by one, small improvements in the levelized cost of ethanol are obtained. However, if the parameters are optimized at the same time, the levelized cost of 0.61 €/L is achieved. Moreover, if the CAPEX is decreased to 75 % from the original value, the result is the levelized cost of 0.54 €/L. Both of these values are more competitive to the current ethanol market price, but it should be noted that the calculated levelized costs do not contain taxation. However, this indicates that a profitable process can possibly be achieved if various parameters are improved at the same time yet there remain challenges, such as a long payback period, which need to be considered and critically evaluated.

Anyway, the results contain uncertainty. In this thesis, the calculations are done by Excel and are mainly based on the simple reaction equations found in literature. Therefore, there are many assumptions and simplifications that must have been included. The calculations give approximate results, but for more accurate analysis, it would be advisable to perform the same analysis with some simulations tool, for instance. Probably, the results are too promising, because they are based on theoretical information and simulations, where the conditions are optimized and real-life surprises do not occur. On the other hand, more detailed analysis of the heat optimization would decrease the energy consumption. The excess heat from the water electrolysis can be utilized for heating in the carbon capture unit, for instance.

For more accurate analysis at least the following issues should be taken into account. In the RWGS unit, the conversion of $CO_2$ is calculated in the dependence on the process temperature, even though in reality it is dependent on the temperature, pressure and the chosen catalyst, for instance. As for the fermentation, the conversion of carbon source

to ethanol depends on how much of the carbon is used for the biomass growth and cell maintenance by the bacteria and it is dependent on the used species. Here, the detailed values for the used bacteria were not found and therefore some general values are used. Additionally, in the calculations, the conversions of the fermentation stage are a combination of information from multiple references and therefore it can be possible that too optimal values are selected. The possible inhibitors, other than high ethanol concentration, are not considered even though in reality some of the syngas impurities may have an inhibitive effect on bacteria. Also, most of the fermentation information is based on theoretical simulations or laboratory scale measurements, which may not be applicable directly to the industrial scale process. Lastly, one significant issue related to the fermentation unit is the produced $CO_2$. Per one kilogram of captured $CO_2$, 0.40 kg of $CO_2$ is produced in the fermenter. Here, a recovery stream from the fermenter to the RWGS unit is not calculated, since it requires additional treatment steps. However, for the more optimized process it must be included. It is not sensible to create a $CO_2$ capturing process, which at the same time releases $CO_2$ as a by-product. This change to the process will decrease the costs from the carbon capture unit, but at the same time the required treatment steps cause additional costs.

As for the CAPEX, a more accurate data are required. Here, the results are based on quite approximate values, since all the unit processes are not mature technology yet and therefore precise data on the investment costs are hard to find. For example, in the case of the carbon capture unit, a comparison between a detailed scientific article and a short newspaper article was done. The scientific article gave costs that are ten times higher than the ones from the newspaper article or the current market prices of the equipment. Therefore, the data from the newspaper article has been chosen since even though it is approximate data it is a realized project rather than a simulation.

In the OPEX calculations, the catalysts for the RWGS and fermentation are not considered due to the lack of cost information. For more accurate analysis, those should be included and they can be assumed to increase the operational expenses and have an effect on the cost distributions. Additionally, the taxation of ethanol should be included and the fixed cost evaluated more carefully. On the other hand, some of the chemical prices are based on small packages even though the consumption is great. The cost of ammonium chloride, for example, is calculated based on the package size of 25 kg while the annual consumption is approximately 60 tons. In reality, the price would be cheaper for the larger and repeated orders. All in all, the assumption that the OPEX is not dependent on the plant size, is a very rough estimation to simplify the calculations. In reality, the scaling of the OPEX would not be linear.

In the scenario analysis, the parameters are varied, but the probability to the scenarios to realize must be considered more. First, one of the examined scenarios is the by-product $O_2$ selling, which is analyzed as a discrete variable: Either all the produced $O_2$ is sold or it is not sold at all. However, the purchaser of the sold $O_2$ is not taken into account, even though pulp and paper industry is one of the largest industrial oxygen users in Finland (Hurskainen 2017). Therefore, it is sensible to assume that before selling externally, the produced $O_2$ would be utilized in the pulp mill and after that the rest would be sold meaning that at the same time the profit decreases but savings in $O_2$ purchasing are achieved.

Secondly, the forecasting of the development of the (renewable) electricity price is complex. At the moment, more efficient and green electricity production and storage technologies are under development and implementation indicating lower prices in the future. At the same time, the electrification will become faster and the electricity demand will increase significantly meaning that according to the law of supply and demand, electricity prices would increase. Additionally, the global economic situation affects the changes in the market prices.

Since the expenses of $H_2$ production by the water electrolyser are highly dependent on the electricity price, the role of that unit process should be considered. It can be expected that the electrolyser technology will progress in the future, but it is unclear how long it takes. As a comparison, the electricity consumption of the electrolyser unit is 71 MW while the produced ethanol (43.5 ML/a) contains little more than 30 MW chemical energy. As long as the electricity consumption of the electrolysers is huge, the end use of the produced ethanol must be critically considered to decide whether it is reasonable to consume that amount of (renewable) energy to such a low-energy end-product. IEA (2020) is expecting that in 2030 the shares of $H_2$ supply are roughly equal between water electrolysis and fossil fuel based process with CCS. Even though the share will move slightly in favour of water electrolysis over time, the $H_2$ production from fossil fuels with CCS will likely remain the cheapest route in most regions and in 2070 it still accounts for 40 % of global hydrogen production. Therefore, it might be sensible to consider the water electrolysis replacement with some other $H_2$ production technology. One possibility is also the purchasing of $H_2$ instead of an own water electrolysis unit. This would increase the OPEX significantly, but at the same time the required capital investment is decreased, which might have a positive effect on the implementation of the process if the decision is questionable.

In addition to the varied parameters in the scenario analysis, there are many issues, which have an effect on the process profitability. The most significant is the development

of the market price of ethanol. Generally, the global industrial grade ethanol production is projected to grow from 116 billion litres to 128 billion litres by 2025 (Beroe). At the same time, more efficient production technologies for the 1st, 2nd and even 3rd generation ethanol are developed. If the trend continues similar, the market price of ethanol will still decrease in the future meaning that the profit earning will become harder (Balat & Balat 2009). On the other hand, in the future, carbon tax or other political decisions may have positive impact on the process profitability. For example, if the captured $CO_2$ is fossil-based, it may be possible to get savings from carbon tax or if it is possible to get compensation from negative carbon balance, extra revenue may be achieved.

Other possibility is to select some other more expensive end-product, which will increase the profit of the process. Gas fermentation is a multi-purpose technology because depending on the used bacteria, the product can vary from ethanol to various chemicals, such as isopropanol, acetate, succinate, butanol and butyrate. However, if the end-product is changed the potential market volume will probably be significantly lower in comparison with ethanol which is a widely used fuel, chemical and solvent. Therefore, a careful investigation of the present and upcoming trends of the selected product must be performed to make sure that the demand is high enough for a feasible business.

# 8. CONCLUSIONS

In this thesis, the purpose was to investigate the carbon capturing and utilization possibilities for biogenic $CO_2$. Since climate change is proceeding rapidly, efficient solutions and technologies to decrease the GHG emissions are under development. Some alternatives are CCS and CCU, from which CCS is a more efficient climate mitigation tool, since it stores the captured $CO_2$ underground permanently but it is an unprofitable business that requires a large capital investment, while CCU may be a successful business since the products can be sold. In this thesis, the purpose was to rather find commercially potential technologies and investigate the feasibility of those than solve the whole global warming issues and therefore, only CCU technologies were considered.

The focus was on the capturing and utilization of biogenic $CO_2$, since by utilizing biogenic $CO_2$ it is possible to reach even negative $CO_2$ balance and the products are considered bioproducts. The main advantage of a bioproduct is that it replaces the counterparts which are made from fossil resources. Even though in CCU the $CO_2$ is not permanently stored or removed from atmosphere, the use of fossil fuels is decreased. The main sources of biogenic $CO_2$ are bioethanol production, anaerobic biogas digesters, pulp mills or biorefineries and waste-to-energy plants. Since pulp and paper industry is one of the largest industrial energy users globally, it was chosen to be the $CO_2$ source of this study together with biomass power plants.

The most significant factors affecting the selection of a suitable carbon capture technology are the volume of flue gas to be treated, $CO_2$ concentration and pressure. In the post-combustion technologies, the main challenges are a relatively low $CO_2$ concentration (typically 10-20 %) and a low pressure, in which case the partial pressure is low and the volume of flue gas large. The main subcategories of PCC technologies include absorption, adsorption, cryogenic, membrane and biological techniques, from which chemical absorption is preferred. Currently, the amine-based chemical absorption is the industrial benchmark of PCC and it is reasonable to suppose that also in the future, most of the PCC technologies are based on chemical absorption process. Since amines have been used for over 60 years in chemical and oil industries, the mechanism and the involved thermodynamics are well-known and therefore the development of new solvents is easier compared with other not so well-known technologies. However, even though the amine-based absorption is currently ahead in the competition, it is expensive in terms

of both capital and operating costs. Therefore, more efficient technologies and solvents are welcome.

One of the promising alternatives, which was also selected to the TEA, is chemical absorption with potassium carbonate solvent. It has advantages such as easy regeneration, low corrosiveness and low tendency to degradation. The reaction rate of the process is, however, slow and therefore an effective promoter is required to make the process feasible. Carbonic anhydrase as an enzyme has several benefits compared with chemical catalysts and by using CA in the PC solution, it is possible to increase the $CO_2$ absorption by 6-20 fold.

After the capturing, there are multiple utilization possibilities, which are typically divided into chemical and biological conversion, mineralization and direct utilization meaning that the captured $CO_2$ can be utilized as a building block for the production of chemicals or fuels or it can be used directly as it is. However, the end-products are either high added value products with low market volume or low added value products that have a significant market. Both high added value and high market volume cannot be achieved simultaneously. One of the main factors affecting this classification is the presence of hydrogen. Since renewable $H_2$ is typically the most expensive component in CCU products, they can be divided into products which are converted from $CO_2$ with and without $H_2$. The products made without $H_2$ are almost every time more cost-effective, but at the same time the market price of these products is low. If high added value products are desired, they usually require $H_2$ as the second raw material.

In this thesis, the main focus on utilization technologies was set on ethanol, methanol and polyols, because these are products with numerous uses and the markets are stable or expected to grow in the future. Especially, bioethanol production through gas fermentation is a potential technology to both CCU and broader circular economy systems and therefore it was selected to the TEA. Possible origins for the gas substrate in addition to captured $CO_2$ blended with $H_2$ include syngas from gasification of lignocellulosic biomass or municipal solid waste, exhaust gas from steel production and reformed biogas.

In the techno-economic analysis, the aim was to investigate a process of industrial grade bioethanol production through gas fermentation using captured $CO_2$ as a raw material. The process consists of five unit processes, which are carbon capture, water electrolysis, reverse water gas shift, gas fermentation and product recovery. Through these unit processes, the $CO_2$ is first captured from the flue gas, combined with renewable $H_2$ and converted to syngas, which is then fermented to aqueous ethanol broth and finally the

broth is recovered with distillation and molecular sieves to obtain industrial grade (99.5 wt-%) ethanol. The results showed that in the base case the process is definitely not competitive to conventional bioethanol market prices, while in the optimized conditions the levelized cost of ethanol is decreased but for example the discounted payback period of the process is still too high for a feasible investment.

Most of the costs are caused by the water electrolysis unit. Therefore, if the $H_2$ production unit was more cost-efficient, the studied process might be economically feasible. Actually, this is the situation in most of the CCU processes. Since many $CO_2$-based products require $H_2$ for the second raw material, the cost-efficient renewable $H_2$ production has a crucial role in the CCU technologies spreading. However, despite the fact, that the production of renewable $H_2$ is a widely examined research topic, the breakthroughs keep researchers waiting. Therefore, financial inducements for renewable $H_2$ production and $CO_2$ capturing would accelerate the spreading.

However, also the companies themselves can affect the profitability of the process with the selection of the end-product. It can be expected that the first establishing CCU technologies produce high added value products, such as formic acid, in order that the payback period of the investment is realistic, while the low added value products will take more time. Also for this purpose, gas fermentation is a potential technology because depending on the used bacteria, the product can vary from ethanol to various chemicals, such as isopropanol, acetate, butanol and butyrate. Therefore, it might be sensible to first promote gas fermentation with some other more high-priced chemical to obtain more profit. However, since the most significant issues of the process are related to $H_2$, the other quite easy possibility is to just simply focus on products and technologies which do not require additional $H_2$ as the raw material.

Therefore, in the future, the are two possible routes to go ahead. If the processes without additional $H_2$ are promoted, the main issue is to find end-products or direct utilization applications with maximal added value to ensure that the expenses of carbon capturing are covered. On the other hand, if the focus is wanted to keep on gas fermentation, process parameters, such as the solubility of the substrate gases into the solvent and concentration of the end-product in the fermentation broth, must be studied and improved to make the process more efficient.

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